Construction of atropisomeric benzoxepinone-embedded styrenes via intramolecular [3+2] cycloaddition and catalytic kinetic resolution

Yue Wang, Xingfu Wei, Aiqi Xue, Yue Huang, Jingping Qu and Baomin Wang*

State Key Laboratory of Fine Chemicals, Department of Pharmaceutical Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China
Email: bmwang@dlut.edu.cn

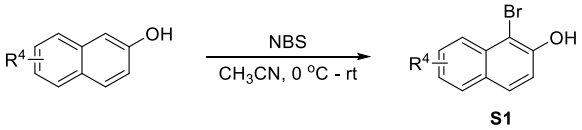
Content

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Diastereoisomeric ratios (dr) were determined by ^{1}H NMR. Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated at 30 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]_D^T$ (c g/100 mL, solvent). All ^{1}H NMR spectra were recorded on Bruker Avance II 400 MHz or Bruker Avance III 600 MHz. ^{19}F NMR spectra were recorded on Bruker Avance II 376 MHz and Bruker Avance III 565 MHz. ^{13}C NMR spectra were recorded on Bruker Avance II 101 MHz or Bruker Avance III 151 MHz with chemical shifts reported as ppm (in $CDCl_3$, TMS as internal standard). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XLTM).

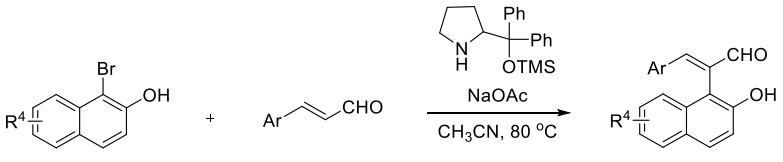
3-Amino oxindole hydrochlorides **4** were prepared according to literature methods.[1] 4-Amino pyrazolone hydrochlorides **2** were prepared following the reported procedures.[2]

2. General procedure for (*E*)-α-aryl enal derivatives 1



S1

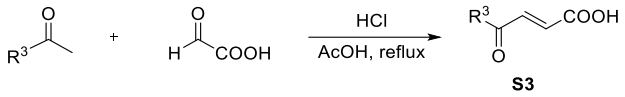
In an oven dried flask, 2-hydroxynaphthalene (1 equiv) was dissolved in CH_3CN (0.3 M). NBS (1 equiv) was added to the mixture at 0 °C. Then, the reaction mixture was gradually warmed up to room temperature and stirred. After the reaction was completed, the solvents were removed. The crude product was then purified by chromatography on silica gel (petroleum ether/ethyl acetate) to give **S1**.



S1 **S2**

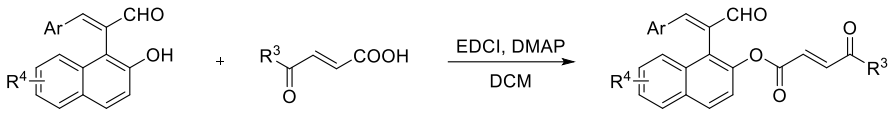
Compound **S2** was prepared according to the literature.[3] To a solution of **S1** (1.0 equiv), cinnamaldehyde (2.0 equiv) and NaOAc (4.0 equiv) in CH_3CN (0.2 M) was added diphenylprolinol TMS ether Cat. (0.1 equiv) under nitrogen atmosphere. Then

the reaction mixture was stirred at 80 °C. After the reaction was completed, the mixture was filtered and the filtrate was removed under reduced pressure. The crude product was added with EtOAc and washed with brine. The organic layer was dried with anhydrous Na_2SO_4 and concentrated. The crude product was then purified by chromatography on silica gel (petroleum ether/ethyl acetate) to give **S2**.



S3

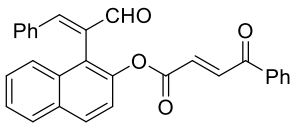
To a solution of methyl ketone (1 equiv) in the mixture of AcOH (0.25 M) and HCl (4 M) was added glyoxylic acid monohydrate (1.5 equiv). The solution was heated to reflux for 18 h. After the reaction was completed, the solvents were removed under reduced pressure. The crude product was then purified by chromatography on silica gel (petroleum ether/ethyl acetate) to give **S3**.



S2 **S3** **1**

To a round-bottom flask with a magnetic stirring bar, **S3** (1.1 equiv), phenol (1 equiv), DMAP (5 mol%) and EDC·HCl (1.1 equiv) were added, and the resulting mixture was stirred in DCM (0.2 M) overnight at room temperature. After the reaction reached completion, H_2O was added. The organic layer was then separated, and the aqueous layer was extracted with EtOAc. The organic layer was successively washed with brine. After drying over Na_2SO_4, the resulting solution was concentrated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel with eluent of petroleum ether/ethyl acetate affording the corresponding pure compound **1**.

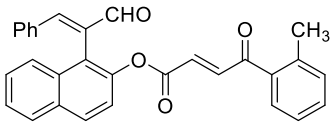
Compound 1a



1a

Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 15.5 Hz, 1H), 7.80 (s, 1H), 7.65-7.60 (m, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.53-7.47 (m, 3H), 7.45 (d, J = 8.9 Hz, 1H), 7.41-7.37 (m, 1H), 7.25-7.22 (m, 1H), 7.15-7.11 (m, 4H), 6.91 (d, J = 15.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 189.0, 163.4, 152.2, 145.9, 137.9, 136.4, 135.1, 134.1, 133.5, 132.0, 131.5, 131.2, 131.0, 130.7, 130.4, 129.0, 128.9, 128.7, 128.6, 127.3, 126.2, 124.9, 122.7, 121.4; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{20}NaO_4^+$ ($[M+Na]^+$) 455.1254, Found 455.1254.

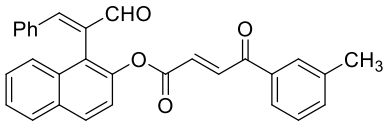
Compound 1b



1b

Orange solid; mp 72.2-72.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.98 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.80 (s, 1H), 7.61-7.51 (m, 3H), 7.49-7.34 (m, 4H), 7.31-7.24 (m, 2H), 7.24-7.19 (m, 1H), 7.14-7.07 (m, 4H), 6.72 (d, J = 15.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 192.7, 163.5, 152.3, 145.9, 141.1, 138.9, 136.5, 135.0, 133.5, 132.2, 132.1, 132.0, 131.5, 131.2, 131.0, 130.7, 130.4, 129.5, 128.7, 128.6, 127.4, 126.2, 125.9, 124.9, 122.6, 121.4, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{22}NaO_4^+$ ([M+Na]$^+$) 469.1410, Found 469.1419.

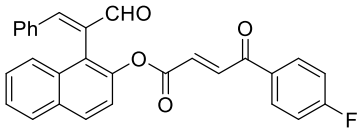
Compound 1c



1c

Orange oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 15.5 Hz, 1H), 7.82-7.77 (m, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.50-7.36 (m, 5H), 7.25-7.22 (m, 1H), 7.17-7.10 (m, 4H), 6.91 (d, J = 15.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 189.2, 163.5, 152.3, 145.9, 138.9, 138.1, 136.4, 135.1, 134.9, 133.5, 132.0, 131.5, 131.0, 131.0, 130.7, 130.4, 129.4, 128.9, 128.7, 128.6, 127.4, 126.2, 126.2, 124.9, 122.7, 121.4, 21.4; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{22}NaO_4^+$ ([M+Na]$^+$) 469.1410, Found 469.1403.

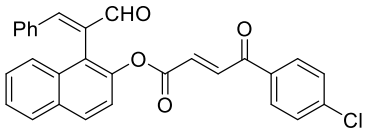
Compound 1d



1d

Light yellow solid; mp 79.3-79.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.02-7.97 (m, 3H), 7.93 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 15.5 Hz, 1H), 7.80 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.50-7.47 (m, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.41-7.36 (m, 1H), 7.26-7.24 (m, 1H), 7.20-7.16 (m, 2H), 7.14 (d, J = 4.4 Hz, 4H), 6.92 (d, J = 15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 187.3, 166.3 (d, J = 256.7 Hz), 163.3, 152.2, 145.9, 137.43, 135.0, 133.5, 132.8 (d, J = 3.0 Hz), 132.0, 131.7 (d, J = 10.6 Hz), 131.5, 131.4, 131.0, 130.7, 130.4, 128.7, 128.6, 127.4, 126.3, 124.9, 122.7, 121.3, 116.3 (d, J = 22.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.89; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}FNaO_4^+$ ([M+Na]$^+$) 473.1160, Found 473.1150.

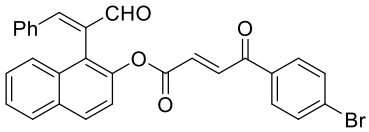
Compound 1e



1e

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.95-7.86 (m, 3H), 7.86-7.78 (m, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.51-7.42 (m, 4H), 7.42-7.35 (m, 1H), 7.26-7.22 (m, 1H), 7.16-7.10 (m, 4H), 6.92 (d, J = 15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 187.7, 163.3, 152.2, 145.9, 140.7, 137.2, 135.0, 134.7, 133.5, 132.0, 131.7, 131.5, 131.0, 130.7, 130.4, 130.3, 129.4, 128.8, 128.6, 127.4, 126.3, 124.9, 122.7, 121.3; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}ClNaO_4^+$ ($[M+Na]^+$) 489.0864, Found 489.0869.

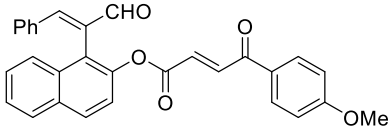
Compound 1f



1f

Light yellow solid; mp 97.2-97.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.86-7.77 (m, 4H), 7.64 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.4 Hz, 1H), 7.50-7.42 (m, 2H), 7.41-7.36 (m, 1H), 7.25-7.21 (m, 1H), 7.16-7.09 (m, 4H), 6.92 (d, J = 15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.7, 187.9, 163.3, 152.2, 145.9, 137.2, 135.1, 135.0, 133.5, 132.4, 132.0, 131.7, 131.5, 131.0, 130.7, 130.4, 130.3, 129.6, 128.8, 128.6, 127.4, 126.3, 124.9, 122.7, 121.3; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}BrNaO_4^+$ ($[M+Na]^+$) 533.0359, Found 533.0350.

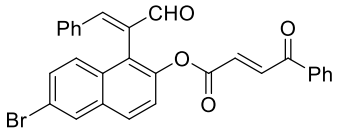
Compound 1g



1g

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.01-7.85 (m, 5H), 7.79 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.50-7.41 (m, 2H), 7.40-7.33 (m, 1H), 7.24-7.20 (m, 1H), 7.15-7.08 (m, 4H), 6.95 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 15.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 187.1, 164.4, 163.6, 152.3, 146.0, 138.1, 135.1, 133.5, 132.0, 131.6, 131.4, 131.0, 130.7, 130.5, 130.3, 129.5, 128.7, 128.6, 127.3, 126.2, 125.0, 122.7, 121.5, 114.3, 55.6; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{23}O_5^+$ ($[M+H]^+$) 463.1540, Found 463.1536.

Compound 1h

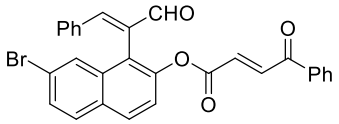


1h

Light yellow solid; mp 91.2-92.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.07 (s, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.91 (s, 1H), 7.88 (d, J = 6.0 Hz, 1H), 7.80 (s, 1H), 7.65-7.58 (m, 1H), 7.54-7.40 (m, 5H), 7.27-7.23 (m, 1H), 7.18-7.08 (m, 4H), 6.91 (d, J = 15.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 188.9, 163.3, 152.7, 146.2, 138.1, 136.3, 134.6, 134.1, 133.3, 133.1, 131.2, 131.0,

130.7, 130.6, 130.1, 129.4, 129.0, 128.9, 128.8, 126.8, 123.1, 122.7, 120.4; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}BrNaO_4^+$ ([M+Na]$^+$) 533.0359, Found 533.0354.

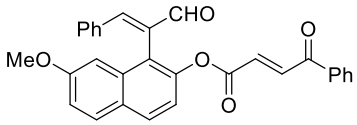
Compound 1i



1i

Orange oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.96-7.90 (m, 3H), 7.87 (d, *J* = 15.5 Hz, 1H), 7.80 (s, 1H), 7.77-7.71 (m, 2H), 7.63-7.57 (m, 1H), 7.52 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.50-7.44 (m, 3H), 7.25 (dd, *J* = 12.1, 5.2 Hz, 1H), 7.17-7.09 (m, 4H), 6.90 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.5, 188.9, 163.3, 153.0, 146.7, 138.1, 136.3, 134.5, 134.2, 133.3, 132.9, 131.2, 131.0, 130.7, 130.4, 130.3, 130.2, 129.7, 129.0, 128.9, 128.9, 127.2, 122.1, 122.0, 122.0; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}BrNaO_4^+$ ([M+Na]$^+$) 533.0359, Found 533.0357.

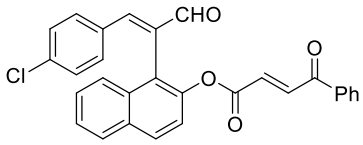
Compound 1j



1j

Light yellow solid; mp 72.7-73.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.99-7.87 (m, 4H), 7.84-7.79 (m, 2H), 7.64 (m, 1H), 7.51 (m, 2H), 7.33-7.26 (m, 2H), 7.19-7.10 (m, 5H), 6.92 (d, *J* = 15.5 Hz, 1H), 6.79 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 189.0, 163.5, 158.8, 151.8, 146.7, 137.8, 136.4, 135.2, 134.1, 133.6, 132.9, 131.3, 131.0, 130.6, 130.2, 130.1, 129.0, 128.9, 128.7, 127.4, 121.4, 118.8, 118.8, 103.5, 55.2; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{23}O_5^+$ ([M+H]$^+$) 463.1540, Found 463.1540.

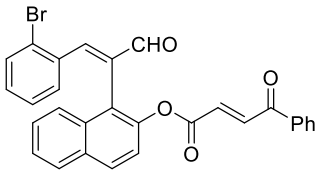
Compound 1k



1k

Light yellow solid; mp 90.6-91.3 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.93-7.88 (m, 2H), 7.73 (s, 1H), 7.63-7.58 (m, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.52-7.46 (m, 3H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.41-7.36 (m, 1H), 7.11-7.03 (m, 4H), 6.93 (d, *J* = 15.5 Hz, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 188.9, 163.5, 150.4, 146.0, 138.0, 137.0, 136.3, 135.4, 134.2, 132.1, 131.9, 131.9, 131.3, 131.1, 130.6, 129.1, 129.0, 128.9, 128.7, 127.5, 126.4, 124.7, 122.4, 121.5; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}ClNaO_4^+$ ([M+Na]$^+$) 489.0864, Found 489.0858.

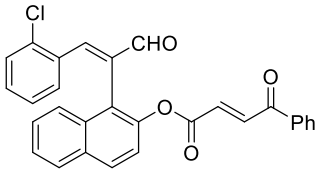
Compound 1l



1l

Yellow solid; mp 93.4-94.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.14 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 2.3 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.67-7.62 (m, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.57-7.51 (m, 3H), 7.50-7.42 (m, 2H), 7.37 (d, J = 8.9 Hz, 1H), 7.08-7.04 (m, 1H), 6.98 (d, J = 15.5 Hz, 1H), 6.87-6.81 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 189.1, 163.5, 150.7, 146.0, 138.1, 136.9, 136.4, 134.1, 133.6, 133.0, 131.9, 131.8, 131.5, 131.2, 130.5, 130.3, 129.0, 129.0, 128.6, 127.4, 127.4, 126.2, 125.4, 124.9, 121.7, 121.3; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{19}BrNaO_4^+$ ([M+Na]$^+$) 533.0359, Found 533.0350.

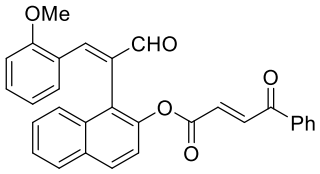
Compound 1m



1m

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.21 (s, 1H), 8.02-7.98 (m, 2H), 7.97-7.87 (m, 3H), 7.67-7.61 (m, 1H), 7.59-7.34 (m, 7H), 7.17-7.11 (m, 1H), 6.95 (d, J = 15.6 Hz, 1H), 6.86-6.82 (m, 1H), 6.81-6.75 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 189.1, 163.4, 148.0, 146.0, 138.1, 137.0, 136.4, 135.0, 134.1, 131.9, 131.9, 131.7, 131.5, 131.1, 130.5, 130.1, 129.7, 129.0, 129.0, 128.6, 127.4, 126.8, 126.2, 124.9, 121.9, 121.3; HRMS (ESI) *m/z* Calcd. for $C_{29}H_{20}ClO_4^+$ ([M+H]$^+$) 467.1045, Found 467.1045.

Compound 1n

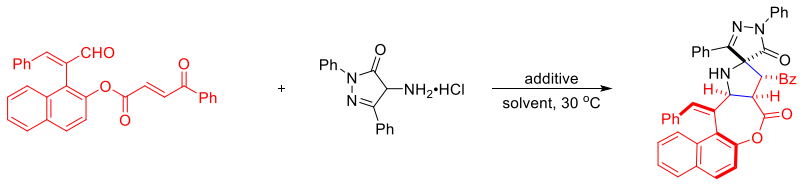


1n

Light yellow solid; mp 86.4-87.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.30 (s, 1H), 8.01-7.85 (m, 5H), 7.67-7.57 (m, 2H), 7.56-7.44 (m, 3H), 7.41 (d, J = 8.8 Hz, 2H), 7.23-7.18 (m, 1H), 6.89 (d, J = 15.5 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 6.76-6.71 (m, 1H), 6.51-6.45 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 189.2, 163.3, 158.1, 147.3, 145.7, 137.6, 136.5, 134.7, 134.1, 132.5, 132.0, 131.8, 131.4, 130.0, 129.8, 129.0, 128.9, 128.5, 127.2, 126.1, 125.2, 123.0, 122.6, 121.4, 120.5, 110.6, 55.6; HRMS (ESI) *m/z* Calcd. for $C_{30}H_{23}O_5^+$ ([M+H]$^+$) 463.1540, Found 463.1539.

3. Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions

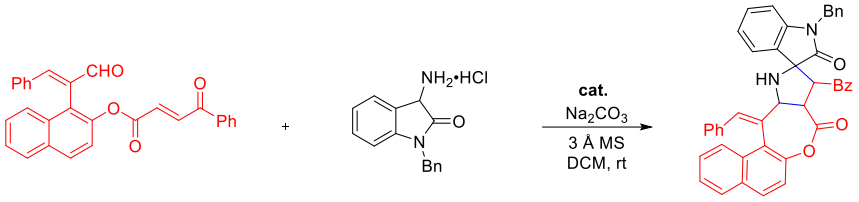


1a **2a** **3aa**

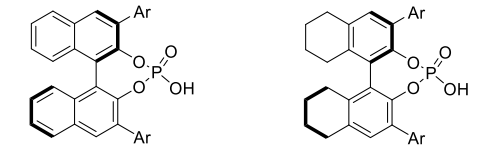
Entry[a]	Additive	Solvent	t [h]	dr[c]	Yield [%][b]
1	3 Å MS	toluene	24	>20:1	48
2	3 Å MS	DCE	15	>20:1	58
3	3 Å MS	$CHCl_3$	24	>20:1	62
4	3 Å MS	DCM	12	>20:1	78
5	3 Å MS	THF	15	>20:1	36
6	3 Å MS	Et_2O	24	>20:1	30
7	3 Å MS	EtOH	24	-	trace
8	-	DCM	48	>20:1	45
9	**4 Å MS**	**DCM**	**10**	**>20:1**	**85**
10	5 Å MS	DCM	10	>20:1	72
11	Na_2SO_4	DCM	10	>20:1	69
12	$MgSO_4$	DCM	10	>20:1	50
13[d]	4 Å MS	DCM	6	>20:1	75
14[e]	4 Å MS	DCM	12	>20:1	80
15[f]	4 Å MS	DCM	10	>20:1	79

[a]Unless otherwise noted, the reaction was carried out on a 0.1 mmol scale in solvent (1.0 mL) at 30 °C under nitrogen, and the ratio of **2a/1a** was 1.3:1. [b]Isolated yield. [c]The dr was determined by ^{1}H NMR of the crude products. [d]In 0.5 mL DCM. [e]In 2.0 mL DCM. [f]Na_2CO_3 (1.3 equiv.) was added.

Table S2. Preliminary asymmetric reaction



1a **4c** **5ac**



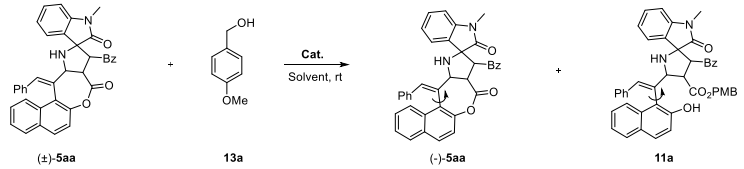
CPA1, Ar = 9-phenanthryl
CPA2, Ar = 3,5-$(CF_3)_2$-C_6H_3

CPA3, Ar = 9-phenanthryl
CPA4, Ar = 9-pyrenyl

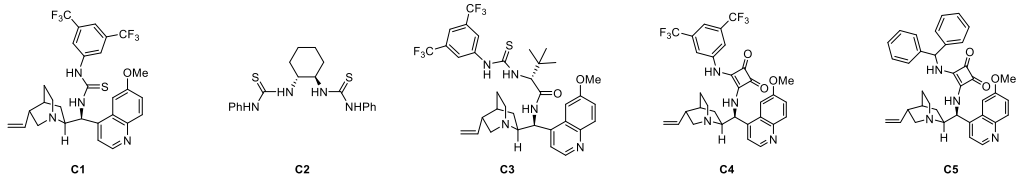
Entry[a]	Cat.	Solvent	t [h]	Yield [%][b]	dr[c]	ee [%][d]
1	**CPA1**	DCM	48	76	>20:1	0
2	**CPA2**	DCM	48	60	>20:1	0
3	**CPA3**	DCM	48	62	>20:1	11
4	**CPA4**	DCM	48	78	>20:1	5
5[e]	**CPA3**	DCM	48	87	>20:1	0

[a] The reaction was carried out on a 0.1 mmol scale with 3 Å MS (100 mg), **CPA** (10 mol%) in 1.0 mL solvent at room temperature under nitrogen, and the ratio of **4c**/**1a** was 1.5/1. [b] Isolated yield. [c] The dr was determined by ^{1}H NMR of the crude reaction mixture. [d] The ee was determined by chiral HPLC. [e] **2a** was used instead of **4c**.

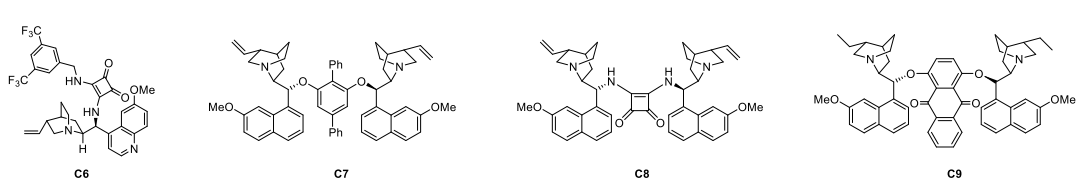
Table S3. Optimization of the KR reaction conditions



(±)-**5aa** **13a** (-)-**5aa** **11a**



C1 **C2** **C3** **C4** **C5**

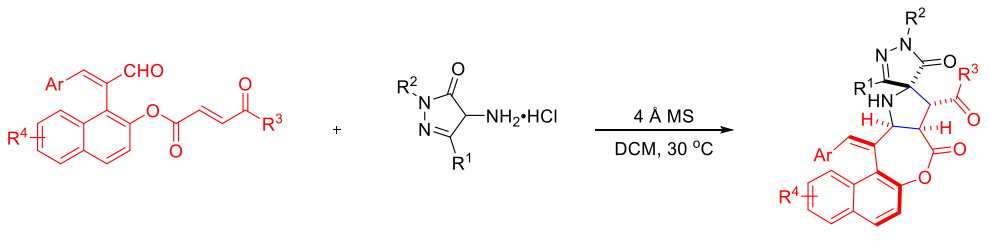


C6 **C7** **C8** **C9**

Entry[a]	Cat.	Solvent	(–)-5aa		11a		C [%][d]	s[e]
			yield [%][b]	ee [%][c]	yield [%][b]	ee [%][c]		
1	**C1**	DCM	52	53	42	43	55	4
2	**C2**	DCM	quant.	-	NR	-	-	-
3	**C3**	DCM	> 95	-	Trace	-	-	-
4	**C4**	DCM	52	82	44	92	47	61
5	**C5**	DCM	65	31	30	85	27	17
6	**C6**	DCM	44	77	42	93	45	64
7	**C7**	DCM	> 95	6	Trace	-	-	-
8	**C8**	DCM	quant.	-	NR	-	-	-
9	**C9**	DCM	quant.	-	NR	-	-	-
10	**C4**	DCE	44	43	31	91	32	32
11	**C4**	$CHCl_3$	48	57	37	95	38	69
12	**C4**	toluene	> 95	10	Trace	-	-	-
13	**C4**	THF	quant.	-	NR	-	-	-
14[f]	**C4**	DCM	50	83	42	93	47	72
15[g]	**C4**	DCM	53	87	46	95	48	111
16[h]	**C4**	DCM	56	69	40	95	42	81
17[g,i]	**C4**	DCM	44	83	54	53	61	8
18[g, j]	**C4**	DCM	56	77	42	89	46	40

[a] The reaction was conducted with (±)-**5aa** (0.12 mmol), **13a** (0.1 mmol) and **Cat.** (10 mol%) in solvent (1.0 mL). [b] Isolated yield. [c] Detected by chiral HPLC analysis. [d] Conversion (C) = ee_s/ (ee_s + ee_p). [e] s = ln [(1-C) (1-ee_s)]/ ln [(1-C) (1+ee_s)]. [f] The ratio of (±)-**5aa**: **13a** = 1.5:1. [g] The ratio of (±)-**5aa**: **13a** = 1:1. [h] The ratio of (±)-**5aa**: **13a** = 0.5:1. [i] With Na_2CO_3 (0.1 mmol). [j] With Et_3N (0.1 mmol).

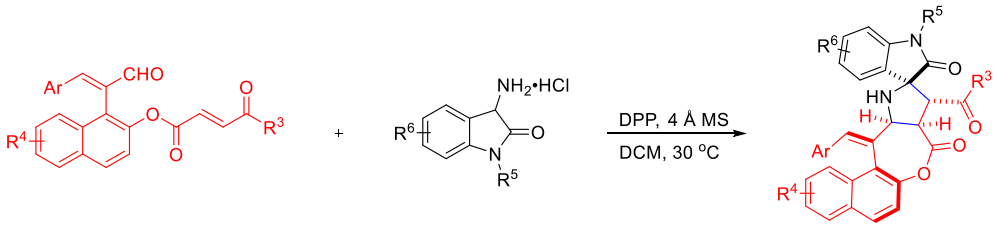
4. General procedure for (±)-3/5



1 2 3

In a Schlenk tube, 4-amino pyrazolone hydrochloride **2** (0.26 mmol), 4 Å MS (200

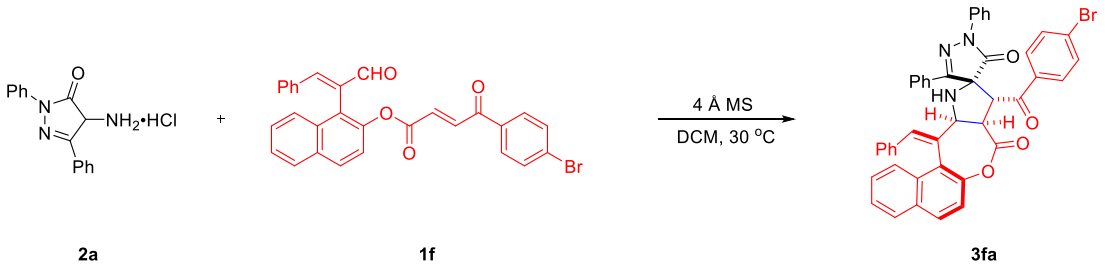
mg) and 1-enal Naphthyl-3-benzoylacrylate **1** (0.2 mmol) were added into DCM (2 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was completed (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/10) on silica gel to give the product **3**.



1 **4** **5**

In a Schlenk tube, 3-amino oxindole hydrochloride **4** (0.26 mmol), 4 Å MS (200 mg), 1-enal Naphthyl-3-benzoylacrylate **1** (0.2 mmol) and DPP (0.02 mmol) were added into DCM (2 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was completed (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **5**.

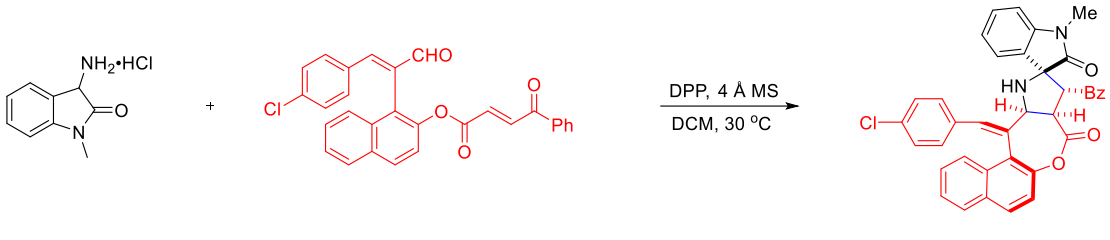
The scale-up reactions



2a **1f** **3fa**

0.57 g, yield = 76%, dr > 20:1

In a Schlenk tube, 4-amino pyrazolone hydrochloride **2a** (1.3 mmol), 4 Å MS (1000 mg) and 1-enal Naphthyl-3-benzoylacrylate **1f** (1.0 mmol) were added into DCM (10 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was completed (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/10) on silica gel to give the product **3fa**.

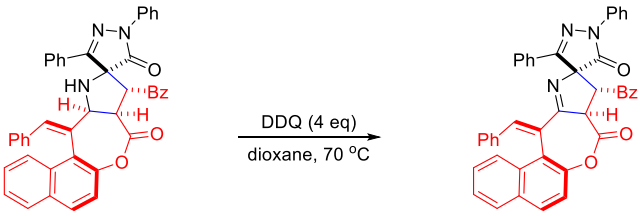


4a **1k** **5ka**

0.41 g, yield = 67%, dr = 10:1

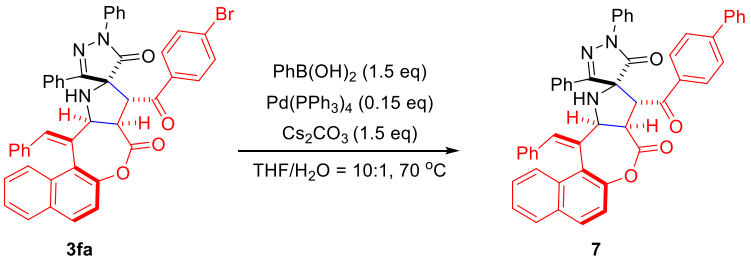
In a Schlenk tube, 3-amino oxindole hydrochloride **4a** (1.3 mmol), 4 Å MS (1000 mg), 1-enal Naphthyl-3-benzoylacrylate **1k** (1.0 mmol) and DPP (0.1 mmol) were added into DCM (10 mL) under nitrogen atmosphere. The reaction solution was stirred at 30 °C. After the reaction was completed (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/5) on silica gel to give the product **5ka**.

Synthetic transformations



3aa **6**

A reaction tube was charged with **3aa** (1.0 equiv, 0.1 mmol) and dioxane (1 mL), and then DDQ (4.0 equiv, 0.4 mmol) was added. The reaction was stirred at 70 °C until it was completed (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **6** as a white solid in 82% yield.

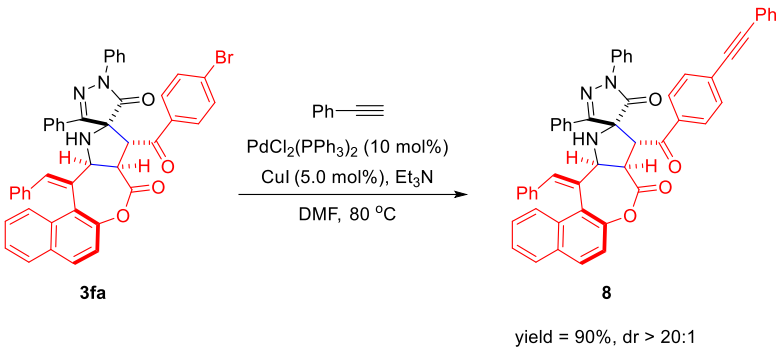


3fa **7**

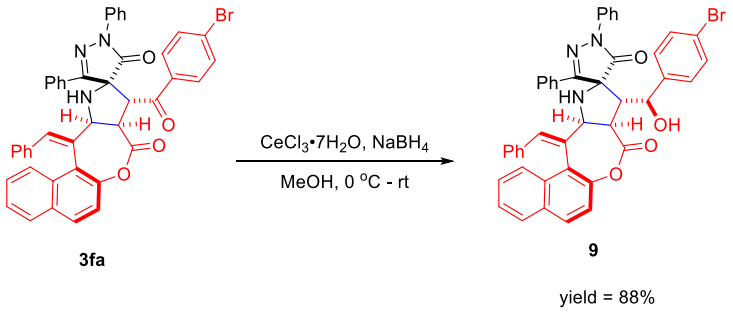
yield = 86%, dr > 20:1

To a solution of **3fa** (1.0 equiv, 0.1 mmol) in 2.0 mL THF/H_2O (10:1) was added phenylboronic acid (1.5 equiv, 0.15 mmol), $Pd(PPh_3)_4$ (0.15 equiv, 0.015 mmol), Cs_2CO_3 (1.5 equiv, 0.15 mmol). Then, the reaction system was degassed and filled with nitrogen for three times. The reaction mixture was stirred under N_2 at 70 °C for 8

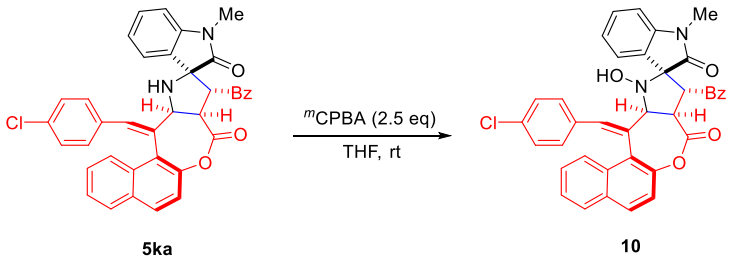
h. After that, the reaction was washed with H_2O and extracted with EA. The combined organic phase was washed with bine and dried with anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford pure product **7** as a yellow solid in 86% yield.



To a solution of **3fa** (1.0 equiv, 0.1 mmol), Et_3N (0.07 mL) in 1.0 mL DMF was added ethynylbenzene (2.5 equiv, 0.25 mmol), CuI (5.0 mol%), $PdCl_2(PPh_3)_2$ (10 mol%). Then, the reaction system was degassed and filled with nitrogen for three times. The reaction mixture was stirred under N_2 at 80 °C for 4 h. After that, the reaction was washed with H_2O and extracted with EA. The combined organic phase was washed with bine and dried with anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford pure product **8** as a yellow solid in 90% yield.



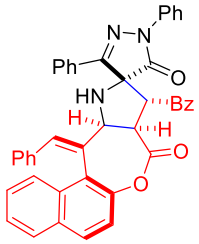
To a solution of **3fa** (1.0 equiv, 0.1 mmol) in MeOH (2.0 mL) was added sodium borohydride (1.2 equiv, 0.12 mmol) and $CeCl_3{\cdot}7H_2O$ (1.2 equiv, 0.12 mmol) at 0 °C for 12 h. The product was purified by silica gel column chromatography to give **9** as white solid in 88 % yield.



A reaction tube was charged with **5ka** (1.0 equiv, 0.1 mmol) and THF (1 mL), then *m*-CPBA (2.5 equiv, 0.25 mmol) was added. The reaction was stirred at room temperature until it was completed (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **10** as a white solid in 93% yield.

Characterization Data

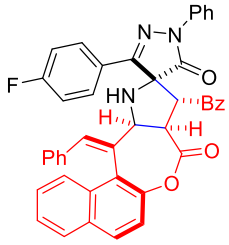
Compound 3aa



3aa

White solid, 85% yield, 113.2 mg; mp 156.7-157.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.8 Hz, 2H), 7.95 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.64-7.57 (m, 3H), 7.53 (d, J = 8.2 Hz, 2H), 7.46-7.33 (m, 6H), 7.33-7.26 (m, 2H), 7.19-7.10 (m, 4H), 7.08-6.98 (m, 3H), 6.98-6.93 (m, 2H), 5.65-5.57 (m, 1H), 5.51 (d, J = 5.0 Hz, 1H), 4.53 (dd, J = 9.7, 5.0 Hz, 1H), 2.76 (d, J = 4.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 173.2, 170.9, 155.7, 147.2, 137.1, 136.3, 135.1, 133.5, 131.6, 131.2, 130.6, 130.4, 130.1, 129.5, 129.2, 128.8, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 127.3, 126.1, 125.5, 125.3, 124.6, 119.1, 118.9, 72.1, 65.6, 56.0, 47.3; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{32}N_3O_4^+$ ([M+H]$^+$) 666.2387, Found 666.2379.

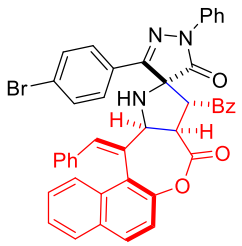
Compound 3ab



3ab

White solid, 82% yield, 112.1 mg; mp 260.4-261.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (dd, J = 8.6, 5.4 Hz, 2H), 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.48-7.39 (m, 5H), 7.38-7.34 (m, 1H), 7.33-7.28 (m, 4H), 7.21-7.14 (m, 3H), 7.10-7.01 (m, 4H), 6.96 (d, J = 7.5 Hz, 2H), 5.67-5.59 (m, 1H), 5.46 (d, J = 4.9 Hz, 1H), 4.51 (dd, J = 9.7, 4.9 Hz, 1H), 2.78 (d, J = 3.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 173.1, 171.0, 164.5 (d, J = 253.5 Hz), 154.9, 147.2, 137.0, 136.3, 135.0, 133.6, 131.6, 130.7, 130.3, 130.1, 129.7, 129.6, 128.8, 128.7, 128.5, 128.3, 128.2 (d, J = 2.0 Hz), 128.0, 127.8, 127.7, 126.2, 125.7 (d, J = 4.0 Hz), 125.5, 125.3, 124.6, 119.1, 118.9, 116.4 (d, J = 22.2 Hz), 72.0, 65.7, 56.0, 47.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -107.70; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}FN_3O_4^+$ ([M+H]$^+$) 684.2293, Found 684.2291.

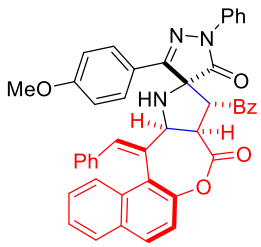
Compound 3ac



3ac

White solid, 78% yield, 116.2 mg; mp 280.2-280.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 7.3, 2.2 Hz, 2H), 7.95 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.64-7.58 (m, 3H), 7.53 (d, J = 7.9 Hz, 2H), 7.47-7.39 (m, 4H), 7.36 (d, J = 8.5 Hz, 1H), 7.33-7.27 (m, 2H), 7.19-7.10 (m, 4H), 7.07-6.99 (m, 3H), 6.98-6.93 (m, 2H), 5.67-5.56 (m, 1H), 5.51 (d, J = 5.1 Hz, 1H), 4.52 (dd, J = 9.7, 5.1 Hz, 1H), 2.77 (d, J = 4.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 173.2, 170.8, 155.7, 147.3, 137.2, 136.4, 135.1, 133.5, 131.6, 131.2, 130.6, 130.4, 130.1, 129.5, 129.1, 128.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.7, 127.7, 127.3, 126.1, 125.4, 125.3, 124.6, 119.1, 118.9, 72.2, 65.6, 56.0, 47.4; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}BrN_3O_4^+$ ($[M+H]^+$) 744.1492, Found 744.1490.

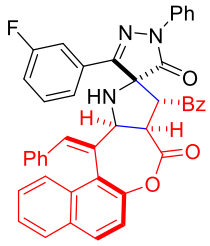
Compound 3ad



3ad

White solid, 80% yield, 111.3 mg; mp 269.4-270.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.9 Hz, 2H), 7.47-7.33 (m, 6H), 7.31-7.26 (m, 2H), 7.20-7.08 (m, 6H), 7.07-6.98 (m, 3H), 6.98-6.90 (m, 2H), 5.62 (d, J = 7.8 Hz, 1H), 5.48 (d, J = 4.7 Hz, 1H), 4.55 (dd, J = 9.4, 4.9 Hz, 1H), 3.93 (s, 3H), 2.74 (d, J = 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 173.0, 171.0, 162.0, 155.6, 147.2, 137.2, 136.3, 135.1, 133.5, 131.6, 130.6, 130.5, 130.1, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 126.1, 125.3, 125.3, 124.6, 122.0, 119.1, 118.9, 114.6, 72.2, 65.8, 56.1, 55.5, 47.2; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{34}N_3O_5^+$ ($[M+H]^+$) 696.2493, Found 696.2485.

Compound 3ae

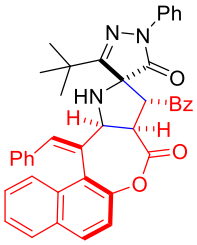


3ae

White solid, 73% yield, 99.8 mg; mp 277.8-278.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 10.0 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.59 (dd, J = 14.4, 7.4 Hz, 1H), 7.52 (d, J = 7.9 Hz, 2H), 7.47-7.38 (m, 5H), 7.37-7.26 (m, 4H), 7.22-7.12 (m, 3H), 7.12-6.99 (m, 4H), 6.98-6.91 (m, 2H), 5.65-5.58 (m, 1H), 5.48 (d, J = 4.6 Hz, 1H), 4.50 (dd, J = 9.3, 4.9 Hz, 1H), 2.77 (d, J = 3.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 173.2, 170.9, 163.1 (d, J = 248.5 Hz), 154.6, 147.2, 137.0, 136.3, 135.0, 133.7, 131.6, 131.5 (d, J = 8.1 Hz), 131.0 (d, J = 8.1 Hz), 130.7,

130.2, 130.1, 128.8, 128.7, 128.5, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 126.2, 125.7, 125.2, 124.6, 123.3 (d, J = 3.0 Hz), 119.1, 118.9, 118.3 (d, J = 21.2 Hz), 113.8 (d, J = 24.2 Hz), 71.9, 65.7, 56.1, 47.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.92; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}FN_3O_4^+$ ($[M+H]^+$) 684.2293, Found 684.2289.

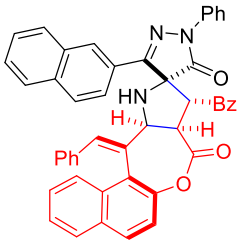
Compound 3af



3af

White solid, 62% yield, 80.1 mg; mp 159.2-159.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.66-7.57 (m, 4H), 7.46 (dd, J = 17.8, 8.1 Hz, 2H), 7.41-7.29 (m, 6H), 7.18-7.12 (m, 1H), 7.11-7.01 (m, 4H), 7.01-6.95 (m, 2H), 5.64 (d, J = 5.3 Hz, 1H), 5.60-5.53 (m, 1H), 4.32 (dd, J = 9.7, 5.4 Hz, 1H), 2.49 (d, J = 4.4 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 173.5, 171.0, 166.3, 147.0, 137.5, 136.9, 135.0, 133.4, 131.6, 130.5, 130.4, 130.08, 128.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.8, 127.7, 126.1, 125.2, 125.0, 124.6, 118.9, 118.5, 73.7, 65.2, 55.9, 48.1, 37.0, 29.4; HRMS (ESI) *m/z* Calcd. for $C_{42}H_{36}N_3O_4^+$ ($[M+H]^+$) 646.2700, Found 646.2696.

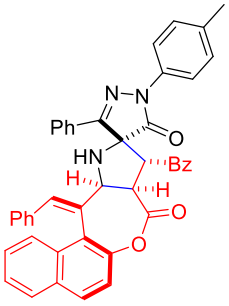
Compound 3ag



3ag

White solid, 72% yield, 103.1 mg; 198.1-198.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.28 (dd, J = 8.7, 1.4 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.99-7.88 (m, 3H), 7.72 (d, J = 8.3 Hz, 1H), 7.64-7.52 (m, 4H), 7.48-7.28 (m, 8H), 7.19-7.09 (m, 4H), 7.08-6.99 (m, 3H), 6.99-6.91 (m, 2H), 5.71-5.60 (m, 2H), 4.60 (dd, J = 9.6, 4.9 Hz, 1H), 2.84 (d, J = 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 173.3, 171.2, 155.6, 147.2, 137.1, 136.3, 135.1, 134.5, 133.6, 133.3, 131.6, 130.7, 130.5, 130.2, 129.8, 128.9, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.0, 126.5, 126.2, 125.6, 125.3, 124.7, 123.2, 119.1, 119.0, 72.2, 66.1, 56.5, 47.5; HRMS (ESI) *m/z* Calcd. for $C_{48}H_{34}N_3O_4^+$ ($[M+H]^+$) 716.2544, Found 716.2537.

Compound 3ah

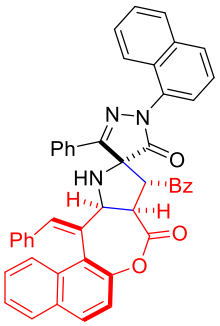


3ah

White solid, 68% yield, 92.4 mg; mp 172.5-173.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41-8.32 (m, 2H), 7.95 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.65-7.54 (m, 3H), 7.47-7.29 (m, 8H), 7.21-7.07 (m, 5H), 7.06-6.90 (m, 5H), 5.61 (d, J = 7.7 Hz, 1H), 5.50 (d, J = 5.0 Hz, 1H), 4.54 (dd, J = 9.7, 5.0 Hz, 1H), 2.75 (d, J = 4.1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 195.6, 173.0, 170.9, 155.5, 147.2, 136.4, 135.3, 135.1, 134.7, 133.5, 131.6, 131.1, 130.6, 130.5, 130.1, 129.6, 129.2, 129.1, 128.8, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 127.3, 126.1, 125.3, 124.7, 119.1, 119.0, 72.1, 65.6, 55.9, 47.3, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{34}N_3O_4^+$ ($[M+H]^+$) 680.2544, Found 680.2539.

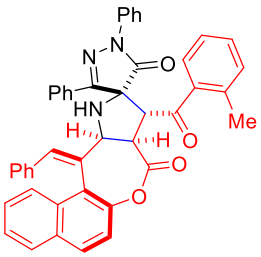
Compound 3ai



3ai

White solid, 71% yield, 101.6 mg; mp 262.3-262.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47-8.42 (m, 2H), 8.07-8.03 (m, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.83-7.77 (m, 3H), 7.75-7.69 (m, 2H), 7.68-7.61 (m, 3H), 7.51-7.41 (m, 6H), 7.41-7.36 (m, 2H), 7.18-7.12 (m, 3H), 7.10-7.02 (m, 3H), 7.01-6.96 (m, 2H), 5.68 (dd, *J* = 9.7, 2.0 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.57 (dd, *J* = 9.8, 5.0 Hz, 1H), 2.84 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 173.4, 170.9, 155.8, 147.2, 136.3, 135.1, 134.7, 133.5, 133.2, 131.6, 131.3, 131.2, 130.6, 130.4, 130.1, 129.5, 129.2, 128.8, 128.5, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 126.5, 126.1, 125.6, 125.3, 124.6, 119.1, 118.2, 116.3, 72.3, 65.7, 56.1, 47.3; HRMS (ESI) *m/z* Calcd. for $C_{48}H_{34}N_3O_4^+$ ($[M+H]^+$) 716.2544, Found 716.2538.

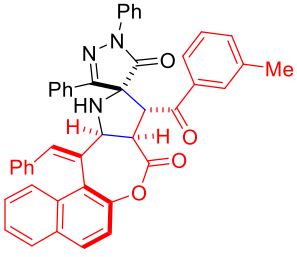
Compound 3ba



3ba

White solid, 80% yield, 108.8 mg; mp 193.5-194.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.28 (m, 2H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.65-7.52 (m, 5H), 7.50-7.42 (m, 2H), 7.40-7.29 (m, 3H), 7.25-7.13 (m, 2H), 7.13-6.94 (m, 8H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.55 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 4.9 Hz, 1H), 4.57 (dd, *J* = 9.7, 5.0 Hz, 1H), 2.73 (d, *J* = 4.0 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 173.2, 170.9, 155.8, 147.3, 138.4, 137.2, 135.6, 135.1, 132.0, 131.6, 131.6, 131.2, 130.6, 130.4, 130.1, 129.5, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.8, 127.7, 127.3, 126.1, 125.4, 125.3, 124.7, 124.6, 119.2, 118.6, 71.6, 65.1, 57.4, 46.8, 19.8; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{34}N_3O_4^+$ ($[M+H]^+$) 680.2544, Found 680.2544.

Compound 3ca

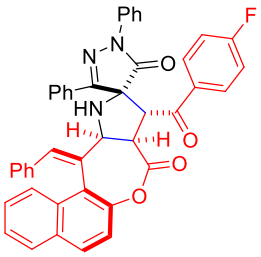


3ca

White solid, 78% yield, 106.0 mg; mp 189.1-189.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.32 (m, 2H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz,

1H), 7.64-7.56 (m, 3H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.46-7.39 (m, 2H), 7.37-7.25 (m, 3H), 7.19-7.08 (m, 5H), 7.07-6.90 (m, 6H), 5.59 (d, *J* = 7.7 Hz, 1H), 5.49 (d, *J* = 5.0 Hz, 1H), 4.56 (dd, *J* = 9.7, 5.0 Hz, 1H), 2.72 (d, *J* = 4.2 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 173.2, 170.9, 155.6, 147.3, 138.3, 137.1, 136.5, 135.1, 134.2, 131.6, 131.2, 130.6, 130.5, 130.1, 129.5, 129.1, 128.8, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.3, 126.1, 125.4, 125.4, 125.3, 124.6, 119.2, 118.8, 72.2, 65.6, 56.1, 47.1, 20.9; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{33}N_3NaO_4^+$ ($[M+Na]^+$) 702.2363, Found 702.2356.

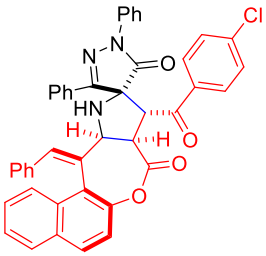
Compound 3da



3da

White solid, 81% yield, 110.8 mg; mp 160.8-161.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.5 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.64-7.52 (m, 5H), 7.47-7.37 (m, 4H), 7.37-7.26 (m, 3H), 7.18-7.08 (m, 2H), 7.08-6.90 (m, 5H), 6.81 (t, *J* = 8.2 Hz, 2H), 5.67-5.53 (m, 1H), 5.46 (d, *J* = 4.9 Hz, 1H), 4.50 (dd, *J* = 9.5, 5.0 Hz, 1H), 2.74 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 173.1, 171.0, 165.9 (d, *J* = 256.5 Hz), 155.6, 147.2, 137.1, 135.1, 132.7, 131.7, 131.4, 131.1, 131.0, 130.7, 130.3, 130.1, 129.4, 129.3, 128.8, 128.6, 128.4, 128.0, 127.9, 127.8, 127.3, 126.2, 125.7, 125.3, 124.6, 119.1, 118.7, 115.5 (d, *J* = 22.2 Hz), 72.2, 65.7, 56.0, 47.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.66; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}FN_3O_4^+$ ($[M+H]^+$) 684.2293, Found 684.2291.

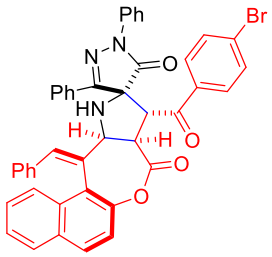
Compound 3ea



3ea

White solid, 75% yield, 105.0 mg; mp 165.9-166.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42-8.36 (m, 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.64-7.56 (m, 3H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.46-7.39 (m, 2H), 7.36-7.28 (m, 5H), 7.18-7.08 (m, 4H), 7.07-6.98 (m, 3H), 6.97-6.89 (m, 2H), 5.63-5.54 (m, 1H), 5.44 (d, *J* = 5.0 Hz, 1H), 4.49 (dd, *J* = 9.7, 5.0 Hz, 1H), 2.75 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 173.1, 170.8, 155.6, 147.2, 140.1, 137.0, 135.0, 134.6, 131.7, 131.4, 130.7, 130.3, 130.1, 129.7, 129.3, 128.8, 128.8, 128.5, 128.3, 128.0, 127.9, 127.8, 127.3, 126.2, 125.6, 125.3, 124.6, 119.1, 118.7, 72.1, 65.7, 56.0, 47.3; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{30}ClN_3NaO_4^+$ ($[M+Na]^+$) 722.1817, Found 722.1810.

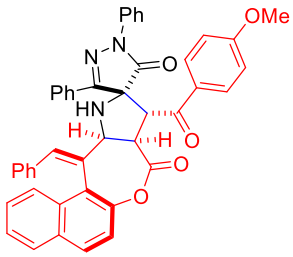
Compound 3fa



3fa

White solid, 80% yield, 119.1 mg; mp 233.2-233.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 7.4, 2.1 Hz, 2H), 7.98 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.67-7.59 (m, 3H), 7.56 (d, J = 7.9 Hz, 2H), 7.49-7.43 (m, 2H), 7.40-7.27 (m, 7H), 7.21-7.12 (m, 2H), 7.10-7.01 (m, 3H), 7.00-6.93 (m, 2H), 5.68-5.58 (m, 1H), 5.46 (d, J = 5.1 Hz, 1H), 4.58-4.42 (m, 1H), 2.79 (d, J = 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 173.1, 170.8, 155.6, 147.2, 137.0, 135.0, 131.7, 131.5, 131.4, 130.7, 130.2, 130.1, 129.8, 129.3, 128.8, 128.8, 128.7, 128.5, 128.3, 128.0, 127.8, 127.8, 127.3, 126.2, 125.6, 125.3, 124.6, 119.1, 118.7, 72.1, 65.7, 56.0, 47.3; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}BrN_3O_4^+$ ([M+H]$^+$) 744.1492, Found 744.1484.

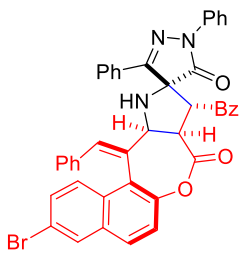
Compound 3ga



3ga

White solid, 85% yield, 118.3 mg; mp 256.2-256.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49-8.41 (m, 2H), 7.97 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.68-7.57 (m, 5H), 7.50-7.42 (m, 4H), 7.41-7.29 (m, 3H), 7.20-7.13 (m, 2H), 7.11-6.95 (m, 5H), 6.66 (d, J = 8.8 Hz, 2H), 5.72-5.63 (m, 1H), 5.51 (d, J = 5.0 Hz, 1H), 4.56 (dd, J = 9.7, 5.0 Hz, 1H), 3.75 (s, 3H), 2.77 (d, J = 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 173.4, 171.0, 163.9, 155.7, 147.3, 137.3, 135.1, 131.6, 131.2, 130.8, 130.6, 130.6, 130.2, 129.6, 129.2, 129.1, 128.8, 128.6, 128.5, 128.3, 127.9, 127.8, 127.7, 127.4, 126.1, 125.4, 125.4, 124.7, 119.1, 118.9, 113.4, 72.3, 65.9, 55.7, 55.4, 47.6; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{34}N_3O_5^+$ ([M+H]$^+$) 696.2493, Found 696.2497.

Compound 3ha

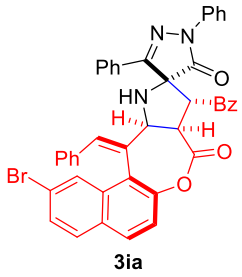


3ha

White solid, 70% yield, 104.2 mg; mp 281.5-281.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.28 (m, 2H), 7.96 (d, J = 1.3 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.62-7.55 (m, 3H), 7.53 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.45-7.34 (m, 4H), 7.31 (dd, J = 9.0, 1.6 Hz, 1H), 7.26-7.22 (m, 2H), 7.18-7.11 (m, 2H), 7.11-6.97 (m, 5H), 6.88 (d, J = 7.1 Hz, 2H), 5.54-5.40 (m, 2H), 4.48 (dd, J = 9.6, 4.9 Hz, 1H), 2.79 (d, J = 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 173.3, 170.6, 155.8, 147.5, 136.9, 136.3, 134.9, 133.6, 132.6, 131.2, 130.9, 130.4, 129.9, 129.7, 129.5, 129.1, 128.7, 128.6, 128.4, 128.4, 128.3,

128.3, 127.9, 127.4, 126.5, 125.6, 125.5, 120.2, 120.2, 119.0, 72.0, 65.5, 56.0, 47.2; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}BrN_3O_4^+$ ($[M+H]^+$) 744.1492, Found 744.1497.

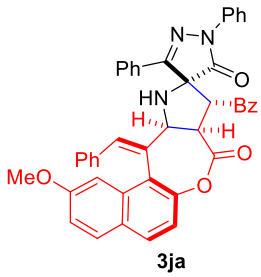
Compound 3ia



3ia

White solid, 70% yield, 104.2 mg; mp 296.1-296.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 4.6 Hz, 2H), 7.93 (d, J = 8.6 Hz, 1H), 7.84 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.66-7.59 (m, 3H), 7.57-7.49 (m, 3H), 7.48-7.38 (m, 4H), 7.35-7.29 (m, 2H), 7.21-7.13 (m, 4H), 7.12-7.03 (m, 3H), 6.96 (d, J = 6.9 Hz, 2H), 5.60 (d, J = 7.5 Hz, 1H), 5.50 (d, J = 4.2 Hz, 1H), 4.59-4.50 (m, 1H), 2.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 173.1, 170.5, 155.6, 148.1, 137.0, 136.3, 134.8, 133.6, 131.4, 131.3, 130.6, 130.1, 130.0, 129.8, 129.6, 129.4, 129.2, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 128.0, 127.3, 126.8, 125.6, 124.6, 122.3, 119.6, 119.0, 72.1, 65.4, 55.9, 47.2; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{31}BrN_3O_4^+$ ($[M+H]^+$) 744.1492, Found 744.1489.

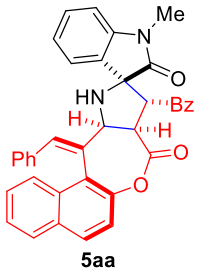
Compound 3ja



3ja

White solid, 68% yield, 94.6 mg; mp 283.5-286.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 4.6 Hz, 2H), 7.86 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.65-7.57 (m, 3H), 7.54 (d, J = 8.0 Hz, 2H), 7.45-7.37 (m, 3H), 7.34-7.27 (m, 3H), 7.21-7.13 (m, 3H), 7.12-6.96 (m, 7H), 6.90 (s, 1H), 5.60 (d, J = 7.6 Hz, 1H), 5.51 (d, J = 4.6 Hz, 1H), 4.54 (dd, J = 9.0, 4.9 Hz, 1H), 3.60 (s, 3H), 2.81 (d, J = 3.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 173.2, 170.9, 159.0, 155.7, 148.0, 137.1, 136.3, 135.2, 133.5, 131.4, 131.2, 130.8, 130.2, 129.9, 129.4, 129.2, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.3, 127.0, 125.5, 124.0, 118.9, 118.8, 116.6, 103.1, 72.1, 65.5, 56.1, 55.2, 47.2; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{33}N_3NaO_5^+$ ($[M+Na]^+$) 718.2312, Found 718.2307.

Compound 5aa

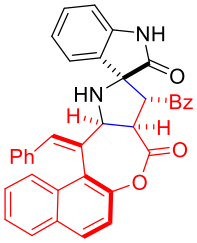


5aa

White solid, 72% yield, 83.0 mg, dr = 15:1; mp 183.3-183.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51-7.41 (m, 2H), 7.40-7.31 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.14 (m, 2H), 7.10-7.04 (m, 2H), 7.03-6.93 (m, 4H), 6.92-6.82 (m, 3H), 6.34 (d, J = 7.8 Hz, 1H), 5.48 (d, J = 4.3 Hz, 1H), 5.03 (t, J = 9.7 Hz, 1H), 4.58 (dd, J = 9.0, 4.3 Hz, 1H), 3.16 (d, J = 12.7 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 175.3, 170.2, 147.8, 143.0, 136.5, 134.8, 132.8, 131.7, 130.8, 130.0, 129.4, 129.4,

128.8, 128.7, 128.5, 128.2, 127.9, 127.9, 127.8, 127.7, 126.0, 125.4, 125.3, 124.6, 123.0, 119.5, 108.2, 71.6, 70.6, 59.2, 49.9, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{29}N_2O_4^+$ ([M+H]$^+$) 577.2122, Found 577.2125.

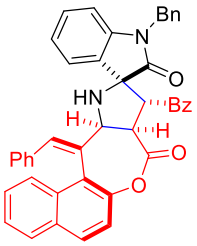
Compound 5ab



5ab

White solid, 45% yield, 50.6 mg, dr = 4:1; mp 180.5-181.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.82 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51-7.38 (m, 5H), 7.38-7.33 (m, 1H), 7.24-7.19 (m, 2H), 7.08 (s, 1H), 7.05-6.94 (m, 5H), 6.92-6.83 (m, 3H), 6.51 (d, J = 7.7 Hz, 1H), 5.53 (d, J = 4.0 Hz, 1H), 5.07-5.01 (m, 1H), 4.59 (dd, J = 8.9, 4.1 Hz, 1H), 3.11 (d, J = 12.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 177.1, 170.3, 147.8, 139.9, 136.4, 134.8, 133.1, 131.7, 130.8, 130.0, 129.5, 129.5, 128.8, 128.7, 128.5, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 126.1, 126.0, 125.3, 124.6, 123.0, 119.5, 110.0, 71.4, 70.9, 58.4, 50.2; HRMS (ESI) *m/z* Calcd. for $C_{37}H_{27}N_2O_4^+$ ([M+H]$^+$) 563.1965, Found 563.1961.

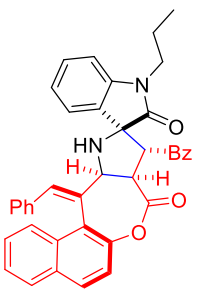
Compound 5ac



5ac

White solid, 50% yield, 65.3 mg, dr > 20:1; mp 190.6-191.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.7 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.50-7.30 (m, 6H), 7.27-7.22 (m, 3H), 7.20-7.07 (m, 5H), 7.04-6.89 (m, 7H), 6.87-6.79 (m, 1H), 6.29 (d, J = 7.5 Hz, 1H), 5.58 (d, J = 3.1 Hz, 1H), 5.15-4.94 (m, 2H), 4.68-4.52 (m, 1H), 4.25 (d, J = 15.5 Hz, 1H), 3.25 (d, J = 12.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 175.6, 170.2, 147.8, 142.3, 136.5, 134.8, 134.8, 133.0, 131.7, 130.8, 130.0, 129.5, 129.4, 128.9, 128.7, 128.5, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.3, 126.1, 125.7, 125.4, 124.6, 123.0, 119.5, 109.4, 71.4, 70.7, 58.5, 50.4, 44.3; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{33}N_2O_4^+$ ([M+H]$^+$) 653.2435, Found 653.2435.

Compound 5ad

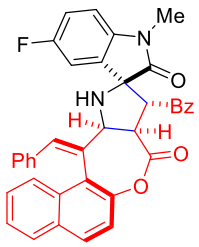


5ad

White solid, 48% yield, 58.1 mg, dr = 12:1; mp 189.3-190.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.51-7.40 (m, 2H), 7.40-7.30 (m, 4H), 7.22-7.14 (m, 2H), 7.11-7.04 (m, 2H), 7.03-6.93 (m, 4H), 6.93-6.80 (m, 3H), 6.42 (d, J = 7.8 Hz, 1H), 5.51 (d, J = 4.4 Hz, 1H), 5.09-4.95 (m, 1H), 4.58 (dd, J = 9.0, 4.4 Hz, 1H), 3.65-3.50 (m, 1H), 3.26-3.10 (m, 2H), 1.57-1.38 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 196.4, 175.2, 170.2, 147.8, 142.7, 136.6, 134.8, 132.9, 131.6, 130.8, 130.0, 129.4, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.0, 125.8, 125.3, 124.6, 122.7, 119.5, 108.6, 71.4, 70.6, 58.6, 50.2, 42.1, 20.6, 11.5; HRMS (ESI) *m/z* Calcd. for $C_{40}H_{33}N_2O_4^+$ ($[M+H]^+$) 605.2435, Found 605.2437.

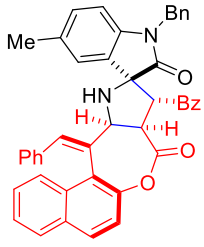
Compound 5ae



5ae

White solid, 58% yield, 69.0 mg, dr = 7:1; mp 208.3-208.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.45-7.32 (m, 5H), 7.24-7.17 (m, 2H), 7.04 (d, *J* = 2.2 Hz, 1H), 7.02-6.94 (m, 3H), 6.92-6.87 (m, 2H), 6.82-6.71 (m, 2H), 6.28 (dd, *J* = 8.5, 4.1 Hz, 1H), 5.49 (d, *J* = 4.3 Hz, 1H), 4.95 (d, *J* = 8.5 Hz, 1H), 4.56 (dd, *J* = 9.0, 4.3 Hz, 1H), 3.18 (s, 1H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 175.1, 170.0, 159.0 (d, *J* = 243.4 Hz), 147.7, 138.9, 136.3, 134.7, 133.0, 131.7, 130.9, 129.9, 129.5, 129.3 (d, *J* = 8.1 Hz), 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 126.1, 125.2, 124.6, 119.4, 115.7 (d, *J* = 23.2 Hz), 113.7 (d, *J* = 25.2 Hz), 108.6 (d, *J* = 8.1 Hz), 71.6, 70.9, 59.1, 49.9, 26.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.15; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}FN_2O_4^+$ ($[M+H]^+$) 595.2028, Found 595.2026.

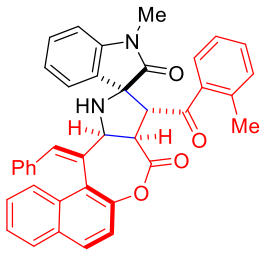
Compound 5af



5af

White solid, 52% yield, 69.3 mg, dr > 20:1; mp 187.2-187.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.50-7.32 (m, 6H), 7.26-7.24 (m, 3H), 7.20-7.09 (m, 5H), 7.03-6.89 (m, 5H), 6.82 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.57 (d, *J* = 4.4 Hz, 1H), 5.10-4.97 (m, 2H), 4.60 (dd, *J* = 9.0, 4.4 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H), 3.25 (d, *J* = 12.8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 175.5, 170.2, 147.9, 139.8, 136.6, 134.9, 134.9, 132.9, 132.7, 131.6, 130.8, 130.0, 129.6, 129.6, 128.8, 128.8, 128.7, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 127.3, 126.3, 126.0, 125.4, 124.8, 119.5, 109.2, 71.5, 70.8, 58.6, 50.4, 44.3, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{45}H_{35}N_2O_4^+$ ($[M+H]^+$) 667.2591, Found 667.2590.

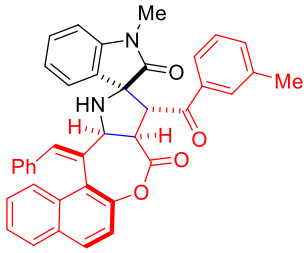
Compound 5ba



5ba

Yellow solid, 60% yield, 70.9 mg, dr = 5:1; mp 190.4-191.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.52-7.44 (m, 2H), 7.44-7.38 (m, 1H), 7.36-7.29 (m, 1H), 7.24-7.11 (m, 3H), 7.06-6.94 (m, 5H), 6.93-6.82 (m, 4H), 6.43 (d, J = 7.8 Hz, 1H), 5.50 (d, J = 5.2 Hz, 1H), 5.00 (t, J = 9.9 Hz, 1H), 4.58 (dd, J = 9.3, 5.3 Hz, 1H), 3.08 (d, J = 12.3 Hz, 1H), 2.82 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 175.0, 170.3, 147.7, 143.1, 139.3, 135.3, 134.8, 131.6, 131.2, 130.8, 129.9, 129.7, 129.4, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 127.8, 127.7, 126.0, 125.3, 125.1, 124.9, 124.6, 123.1, 119.5, 108.4, 70.6, 69.9, 60.3, 49.3, 26.3, 20.1; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{31}N_2O_4^+$ ([M+H]$^+$) 591.2278, Found 591.2271.

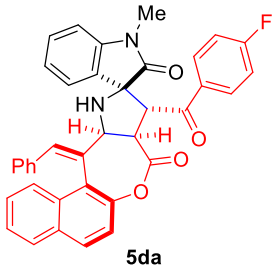
Compound 5ca



5ca

White solid, 72% yield, 85.1 mg, dr = 12:1; mp 200.5-200.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.43-7.37 (m, 1H), 7.34-7.27 (m, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.12-7.03 (m, 4H), 7.02-6.92 (m, 5H), 6.91-6.81 (m, 3H), 6.34 (d, J = 7.8 Hz, 1H), 5.45 (d, J = 4.3 Hz, 1H), 5.03 (t, J = 10.1 Hz, 1H), 4.59 (dd, J = 9.0, 4.3 Hz, 1H), 3.15 (d, J = 12.9 Hz, 1H), 2.94 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 175.3, 170.3, 147.8, 143.1, 137.9, 136.6, 134.9, 133.5, 131.6, 130.8, 130.0, 129.4, 129.3, 128.9, 128.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.8, 127.7, 126.0, 125.4, 125.4, 125.0, 124.6, 122.9, 119.5, 108.1, 71.6, 70.6, 59.3, 49.8, 26.3, 21.1; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{31}N_2O_4^+$ ([M+H]$^+$) 591.2278, Found 591.2277.

Compound 5da

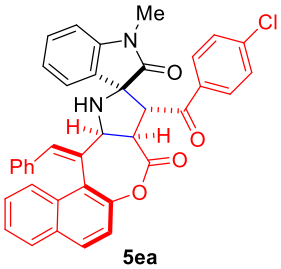


5da

White solid, 68% yield, 80.9 mg, dr = 11:1; mp 198.6-199.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.44-7.38 (m, 1H), 7.37-7.28 (m, 3H), 7.12-7.04 (m, 2H), 7.02-6.92 (m, 4H), 6.91-6.81 (m, 5H), 6.41 (d, J = 7.8 Hz, 1H), 5.43 (d, J = 4.3 Hz, 1H), 5.10-4.97 (m, 1H), 4.57 (dd, J = 9.0, 4.3 Hz, 1H), 3.16 (d, J = 13.2 Hz, 1H), 3.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 175.3, 170.1, 165.5 (d, J = 256.5 Hz), 147.8, 142.9, 134.8, 132.8 (d, J

= 3.0 Hz), 131.6, 130.9, 130.6 (d, *J* = 9.1 Hz), 130.0, 129.6, 129.4, 128.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 126.1, 125.5, 125.3, 124.6, 123.0, 119.5, 115.1 (d, *J* = 22.2 Hz), 108.3, 71.5, 70.6, 59.0, 50.0, 26.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -104.49; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}FN_2O_4^+$ ($[M+H]^+$) 595.2028, Found 595.2028.

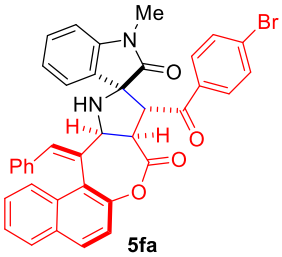
Compound 5ea



5ea

White solid, 65% yield, 79.4 mg, dr = 7:1; mp 205.4-206.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.50-7.41 (m, 2H), 7.37-7.30 (m, 1H), 7.25 (d, *J* = 9.8 Hz, 2H), 7.19-7.13 (m, 2H), 7.13-7.07 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 7.02-6.92 (m, 4H), 6.92-6.83 (m, 3H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.46-5.37 (m, 1H), 5.02 (d, *J* = 8.2 Hz, 1H), 4.55 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.16 (d, *J* = 10.3 Hz, 1H), 3.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 175.2, 170.1, 147.8, 142.9, 139.4, 134.8, 131.7, 130.8, 130.0, 129.6, 129.5, 129.3, 128.7, 128.7, 128.5, 128.2, 128.2, 127.9, 127.7, 127.7, 126.1, 125.5, 125.3, 124.6, 123.1, 119.5, 108.3, 71.5, 70.6, 59.1, 49.9, 26.5; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}ClN_2O_4^+$ ($[M+H]^+$) 611.1732, Found 611.1730.

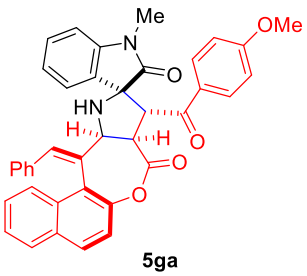
Compound 5fa



5fa

White solid, 70% yield, 91.8 mg, dr = 10:1; mp 262.5-263.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.50-7.38 (m, 2H), 7.37-7.28 (m, 3H), 7.19-7.04 (m, 4H), 7.02-6.82 (m, 7H), 6.42 (d, *J* = 7.8 Hz, 1H), 5.42 (d, *J* = 4.2 Hz, 1H), 5.02 (t, *J* = 10.0 Hz, 1H), 4.55 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.15 (d, *J* = 12.5 Hz, 1H), 2.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 175.2, 170.1, 147.8, 142.9, 135.2, 134.8, 131.6, 131.2, 130.9, 130.0, 129.7, 129.5, 129.4, 128.7, 128.5, 128.2, 128.0, 127.9, 127.7, 127.7, 126.1, 125.5, 125.3, 124.6, 123.1, 119.5, 108.3, 71.5, 70.6, 59.1, 49.9, 26.5; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}BrN_2O_4^+$ ($[M+H]^+$) 655.1227, Found 655.1224.

Compound 5ga

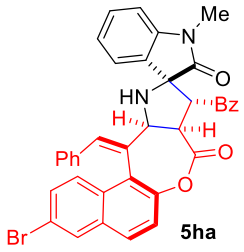


5ga

White solid, 66% yield, 80.1 mg, dr = 9:1; mp 191.2-192.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.50-7.39 (m, 2H), 7.39-7.30 (m, 3H), 7.12-7.03 (m, 2H), 7.03-6.93 (m, 4H), 6.92-6.81 (m, 3H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.42

(d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 4.1 Hz, 1H), 5.04 (s, 1H), 4.58 (dd, *J* = 8.9, 4.2 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 1H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 175.5, 170.3, 163.5, 147.8, 142.9, 134.9, 131.6, 130.8, 130.3, 130.0, 129.4, 129.3, 129.3, 128.9, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 126.0, 125.5, 125.4, 124.6, 122.9, 119.5, 113.2, 108.2, 71.7, 70.9, 58.5, 55.5, 50.2, 26.5; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{31}N_2O_5^+$ ($[M+H]^+$) 607.2227, Found 607.2224.

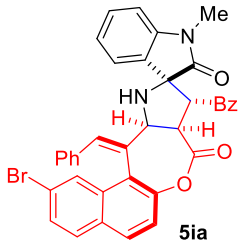
Compound 5ha



5ha

White solid, 64% yield, 83.9 mg, dr > 20:1; mp 230.8-231.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.7 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.41-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.14 (m, 2H), 7.10-7.05 (m, 2H), 7.04-6.92 (m, 4H), 6.90-6.82 (m, 3H), 6.35 (d, *J* = 7.8 Hz, 1H), 5.46 (d, *J* = 4.4 Hz, 1H), 5.00 (t, *J* = 10.2 Hz, 1H), 4.58 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 175.2, 169.9, 148.1, 143.0, 136.4, 134.6, 132.8, 132.7, 131.0, 130.5, 129.8, 129.5, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0 127.9, 127.8, 126.4, 125.6, 125.4, 123.0, 120.7, 120.2, 108.2, 71.4, 70.6, 59.2, 49.8, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}BrN_2O_4^+$ ($[M+H]^+$) 655.1227, Found 655.1224.

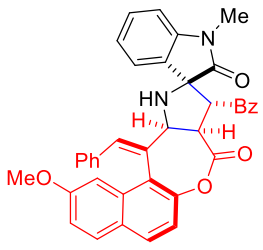
Compound 5ia



5ia

White solid, 58% yield, 76.0 mg, dr = 9:1; mp 220.6-221.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 1.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.51-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.30-7.26 (m, 2H), 7.21-7.14 (m, 2H), 7.11-6.96 (m, 6H), 6.93-6.85 (m, 3H), 6.35 (d, *J* = 7.8 Hz, 1H), 5.46 (d, *J* = 4.3 Hz, 1H), 5.03 (t, *J* = 9.1 Hz, 1H), 4.58 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.14 (d, *J* = 12.7 Hz, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 175.2, 169.8, 148.7, 142.9, 136.4, 134.7, 132.8, 131.2, 130.7, 130.1, 130.0, 129.5, 129.5, 128.5, 128.5, 128.3, 128.0, 128.0, 127.9, 127.8, 126.9, 125.4, 124.6, 123.0, 122.3, 119.9, 108.2, 71.3, 70.6, 59.2, 49.9, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}BrN_2O_4^+$ ($[M+H]^+$) 655.1227, Found 655.1224.

Compound 5ja

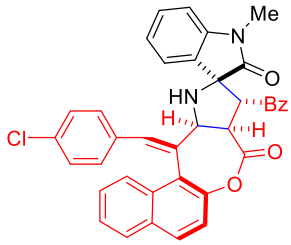


5ja

White solid, 62% yield, 75.2 mg, dr = 12:1; mp 270.3-270.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.40-7.35 (m, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.31-7.27 (m, 2H), 7.21-7.14 (m, 2H), 7.09-7.05 (m, 2H),

7.05-6.91 (m, 8H), 6.90-6.85 (m, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 5.49 (d, *J* = 3.1 Hz, 1H), 5.03 (dd, *J* = 11.9, 10.2 Hz, 1H), 4.62 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.55 (s, 3H), 3.22 (d, *J* = 13.7 Hz, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 175.3, 170.2, 159.1, 148.6, 143.0, 136.5, 135.1, 132.8, 131.2, 130.5, 130.0, 129.5, 129.4, 129.3, 128.4, 128.2, 127.9, 127.9, 127.7, 127.0, 125.6, 124.0, 123.0, 118.9, 117.0, 108.2, 102.8, 71.4, 70.6, 59.3, 55.2, 49.8, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{31}N_2O_5^+$ ($[M+H]^+$) 607.2227, Found 607.2228.

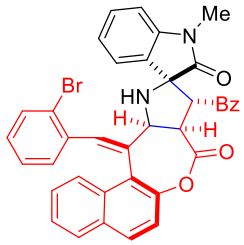
Compound 5ka



5ka

White solid, 72% yield, 88.0 mg, dr = 12:1; mp 272.3-273.6 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.46 (dd, *J* = 16.6, 8.4 Hz, 2H), 7.39-7.32 (m, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.20-7.14 (m, 2H), 7.09-7.04 (m, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.96-6.91 (m, 3H), 6.88-6.83 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.47 (d, *J* = 4.3 Hz, 1H), 5.02 (t, *J* = 10.4 Hz, 1H), 4.59 (dd, *J* = 9.0, 4.3 Hz, 1H), 3.11 (d, *J* = 13.1 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 175.3, 170.0, 147.8, 142.9, 136.4, 133.6, 133.4, 132.8, 131.6, 131.0, 129.9, 129.8, 129.5, 128.6, 128.5, 128.2, 128.0, 127.9, 127.9, 127.8, 126.2, 125.4, 124.8, 124.4, 123.0, 119.5, 108.2, 71.5, 70.5, 59.1, 49.8, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}ClN_2O_4^+$ ($[M+H]^+$) 611.1732, Found 611.1729.

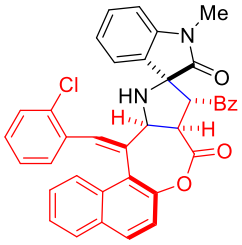
Compound 5la



5la

White solid, 74% yield, 97.0 mg, dr = 10:1; mp 214.5-215.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.9 Hz, 1H), 7.83-7.76 (m, 2H), 7.48-7.32 (m, 5H), 7.32-7.23 (m, 3H), 7.21-7.13 (m, 2H), 7.11-7.01 (m, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.90-6.77 (m, 3H), 6.77-6.69 (m, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 4.4 Hz, 1H), 5.03 (t, *J* = 7.4 Hz, 1H), 4.60 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.09 (d, *J* = 10.5 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 175.3, 170.1, 148.3, 143.0, 136.5, 135.5, 132.8, 132.2, 131.8, 131.4, 130.7, 130.2, 130.0, 129.6, 129.4, 129.1, 128.3, 128.1, 127.9, 127.9, 127.6, 126.9, 126.0, 125.5, 124.6, 124.4, 123.7, 122.8, 119.0, 108.1, 70.8, 70.6, 59.2, 49.7, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}BrN_2O_4^+$ ($[M+H]^+$) 655.1227, Found 655.1226.

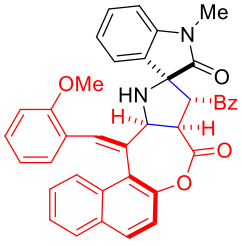
Compound 5ma



5ma

White solid, 67% yield, 81.9 mg, dr = 11:1; mp 271.3-271.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.41-7.33 (m, 3H), 7.32-7.26 (m, 3H), 7.20-7.15 (m, 3H), 7.09-7.04 (m, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.92-6.88 (m, 1H), 6.87-6.83 (m, 1H), 6.80 (d, J = 7.3 Hz, 1H), 6.70-6.65 (m, 1H), 6.33 (d, J = 7.8 Hz, 1H), 5.53-5.42 (m, 1H), 5.04 (t, J = 9.9 Hz, 1H), 4.61 (dd, J = 9.1, 4.4 Hz, 1H), 3.11 (d, J = 12.5 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 175.3, 170.1, 148.3, 143.0, 136.5, 133.7, 133.4, 132.8, 131.8, 131.5, 130.8, 130.1, 129.8, 129.4, 129.0, 129.0, 128.4, 128.0, 127.9, 127.9, 127.6, 127.3, 126.3, 126.0, 125.4, 124.7, 124.3, 122.9, 119.1, 108.2, 71.0, 70.6, 59.2, 49.7, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{28}ClN_2O_4^+$ ($[M+H]^+$) 611.1732, Found 611.1725.

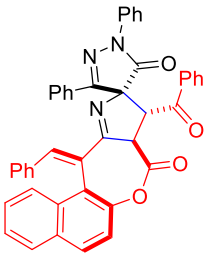
Compound 5na



5na

White solid, 58% yield, 70.4 mg, dr = 10:1; mp 268.8-269.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.41-7.34 (m, 3H), 7.33-7.26 (m, 3H), 7.20-7.13 (m, 2H), 7.08-7.03 (m, 1H), 6.98-6.93 (m, 2H), 6.87-6.82 (m, 1H), 6.67 (dd, J = 13.5, 8.0 Hz, 2H), 6.38-6.30 (m, 2H), 5.48 (d, J = 4.4 Hz, 1H), 5.06-4.98 (m, 1H), 4.58 (dd, J = 9.1, 4.4 Hz, 1H), 3.77 (s, 3H), 3.19 (d, J = 13.3 Hz, 1H) , 2.92 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 175.4, 170.4, 157.1, 148.1, 143.0, 136.6, 132.7, 131.6, 130.4, 130.1, 129.4, 129.1, 128.9, 128.6, 128.3, 128.1, 127.9, 127.9, 127.4, 125.8, 125.8, 125.5, 125.3, 124.7, 124.1, 122.9, 120.0, 119.2, 110.1, 108.1, 71.5, 70.7, 59.4, 55.3, 49.9, 26.4; HRMS (ESI) *m/z* Calcd. for $C_{39}H_{31}N_2O_5^+$ ($[M+H]^+$) 607.2227, Found 607.2235.

Compound 6

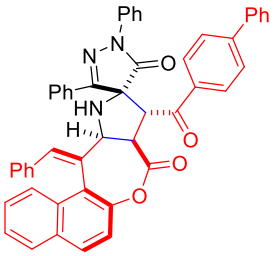


6

White solid, 82% yield, 54.4 mg; mp 210.2-210.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 3.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 1H), 7.61-7.58 (m, 3H), 7.56 (d, J = 8.9 Hz, 1H), 7.47-7.39 (m, 5H), 7.39-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.24-7.17 (m, 4H), 7.14-7.09 (m, 2H), 7.06-7.00 (m, 4H), 5.55 (d, J = 7.7 Hz, 1H), 5.32 (d, J = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 176.8, 168.4,

166.1, 156.5, 146.9, 139.9, 136.8, 136.1, 133.9, 133.8, 132.0, 131.6, 131.3, 130.2, 129.9, 129.9, 129.7, 129.6, 128.5, 128.5, 128.3, 127.9, 126.8, 126.6, 125.7, 125.6, 124.6, 123.4, 120.4, 119.1, 85.3, 56.1, 55.8; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{30}N_3O_4^+$ ($[M+H]^+$) 664.2231, Found 664.2226.

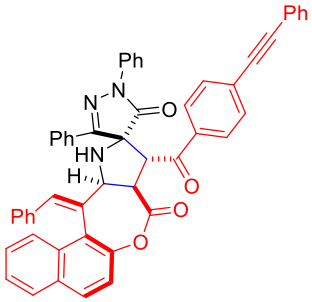
Compound 7



7

Yellow solid, 86% yield, 63.8 mg; mp 261.6-262.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.66-7.57 (m, 3H), 7.52 (d, J = 8.1 Hz, 2H), 7.49-7.38 (m, 9H), 7.38-7.32 (m, 3H), 7.27-7.24 (m, 2H), 7.16-7.10 (m, 2H), 7.09-7.00 (m, 3H), 6.96 (d, J = 7.4 Hz, 2H), 5.63 (d, J = 7.8 Hz, 1H), 5.52 (d, J = 4.8 Hz, 1H), 4.58 (dd, J = 9.7, 4.8 Hz, 1H), 2.77 (d, J = 4.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.3, 173.3, 170.9, 155.8, 147.3, 146.3, 139.7, 137.2, 135.1, 135.0, 131.6, 131.3, 130.6, 130.4, 130.1, 129.5, 129.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.0, 127.8, 127.7, 127.4, 127.3, 126.8, 126.2, 125.4, 125.3, 124.7, 119.2, 118.8, 72.3, 65.8, 56.2, 47.2; HRMS (ESI) *m/z* Calcd. for $C_{50}H_{35}N_3NaO_4^+$ ($[M+Na]^+$) 764.2520, Found 764.2520.

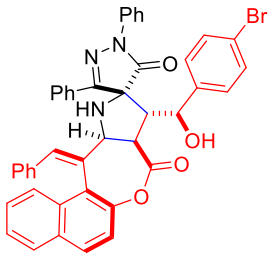
Compound 8



8

Yellow solid, 90% yield, 68.9 mg; mp 280.3-281.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 6.0 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.68-7.60 (m, 3H), 7.60-7.51 (m, 4H), 7.49-7.29 (m, 12H), 7.20-7.12 (m, 2H), 7.10-7.01 (m, 3H), 6.98 (d, J = 6.8 Hz, 2H), 5.65 (d, J = 7.5 Hz, 1H), 5.52 (d, J = 4.9 Hz, 1H), 4.53 (dd, J = 9.6, 5.0 Hz, 1H), 2.79 (d, J = 3.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.8, 173.2, 170.9, 155.6, 147.2, 137.1, 135.3, 135.1, 131.8, 131.6, 131.3, 131.3, 130.7, 130.3, 130.1, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.3, 128.3, 128.0, 127.8, 127.7, 127.3, 126.2, 125.6, 125.3, 124.6, 122.6, 119.1, 119.0, 93.0, 88.5, 72.2, 65.7, 55.9, 47.4; HRMS (ESI) *m/z* Calcd. for $C_{52}H_{35}N_3NaO_4^+$ ($[M+Na]^+$) 788.2520, Found 788.2514.

Compound 9

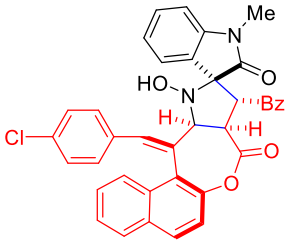


9

White solid, 88% yield, 65.7 mg; mp 270.8-271.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, J = 6.5, 2.8 Hz, 2H), 7.98-7.87 (m, 4H), 7.72 (d, J = 8.3 Hz, 1H), 7.58-7.53 (m, 3H), 7.49-7.42 (m, 3H), 7.40-7.35 (m, 1H), 7.33 (d, J = 8.9 Hz, 1H), 7.27-7.22

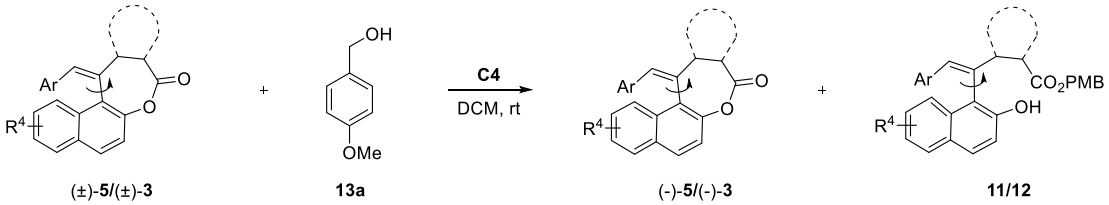
(m, 3H), 7.09-6.99 (m, 4H), 6.99-6.90 (m, 4H), 5.54 (dd, *J* = 9.8, 2.0 Hz, 1H), 4.85-4.73 (m, 1H), 4.43 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.57 (dd, *J* = 9.5, 5.7 Hz, 1H), 2.70 (d, *J* = 4.1 Hz, 1H), 2.59 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 169.9, 157.9, 147.2, 139.6, 137.7, 135.0, 131.5, 130.9, 130.6, 130.2, 130.1, 129.5, 128.9, 128.8, 128.8, 128.5, 128.3, 128.1, 127.9, 127.7, 127.6, 126.1, 125.6, 125.2, 124.6, 122.4, 119.0, 73.1, 72.9, 65.5, 52.2, 48.6; HRMS (ESI) *m/z* Calcd. for $C_{44}H_{32}BrN_3NaO_4^+$ ([M+Na]$^+$) 768.1468, Found 768.1457.

Compound 10



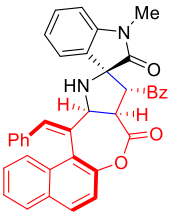
White solid, 93% yield, 58.3 mg; mp 224.3-224.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.53-7.46 (m, 2H), 7.43 (s, 1H), 7.39 (dd, *J* = 11.4, 7.4 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.24-7.11 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.94-6.80 (m, 5H), 6.37 (d, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 5.36 (d, *J* = 6.5 Hz, 1H), 4.80-4.57 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 175.1, 169.0, 147.0, 143.5, 136.6, 133.4, 133.3, 132.9, 131.6, 130.6, 130.1, 130.1, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 126.8, 126.3, 124.8, 124.6, 123.3, 122.9, 119.4, 108.1, 74.6, 72.7, 51.9, 44.0, 26.3; HRMS (ESI) *m/z* Calcd. for $C_{38}H_{27}ClN_2NaO_5^+$ ([M+Na]$^+$) 649.1501, Found 649.1504.

5. General procedure for catalytic kinetic resolution of (±)-3/5



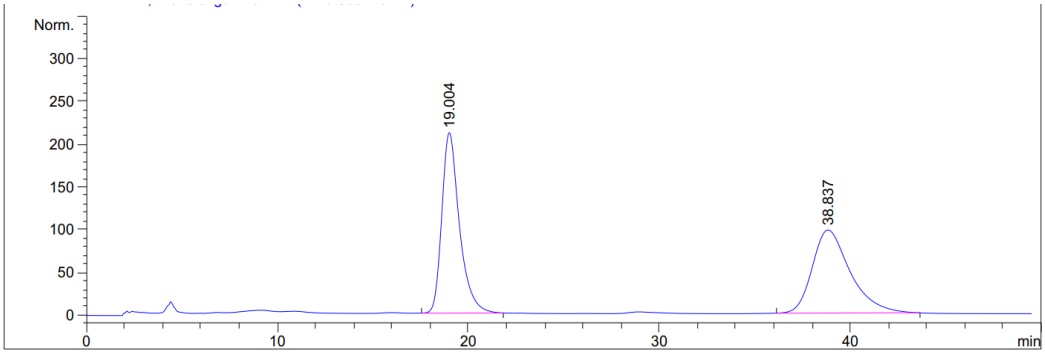
A reaction tube was charged with (±)-**5**/**3** (1.0 equiv, 0.1 mmol) and DCM (1 mL), then benzyl alcohol (1.0 equiv, 0.1 mmol) and **C4** (0.1 equiv, 0.01 mmol) were added. The reaction was stirred at room temperature for 120 h, then the crude product was purified by column chromatography on silica gel to afford the corresponding **11**/**12** and the enantioenriched compound (–)-**5**/(–)-**3**.

KR-Compound (–)-5aa

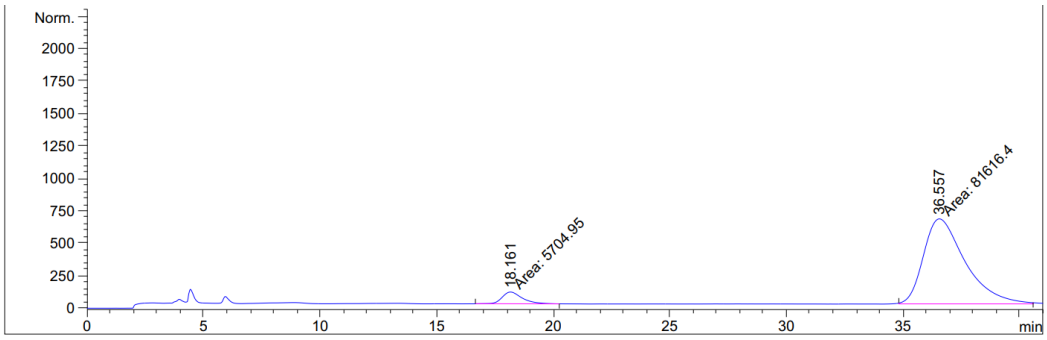


(-)-**5aa**

Prepared according to the procedure within 120 h as white solid (24.8 mg, 43% yield); $[\alpha]_D^{18}$= -81.96 (*c* 0.33, CH_2Cl_2); Enantiomeric excess was determined to be 87% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 36.6 min, t_{minor} = 18.2 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.004	BB	0.9610	1.35380e4	211.02519	50.2160
2	38.837	BB	2.0409	1.34216e4	97.17712	49.7840

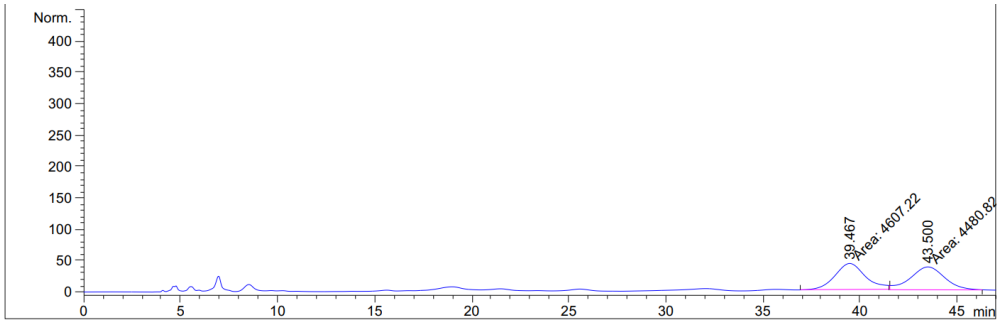


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.161	MM	1.0369	5704.94580	91.69640	6.5333
2	36.557	MM	2.0773	8.16164e4	654.83344	93.4667

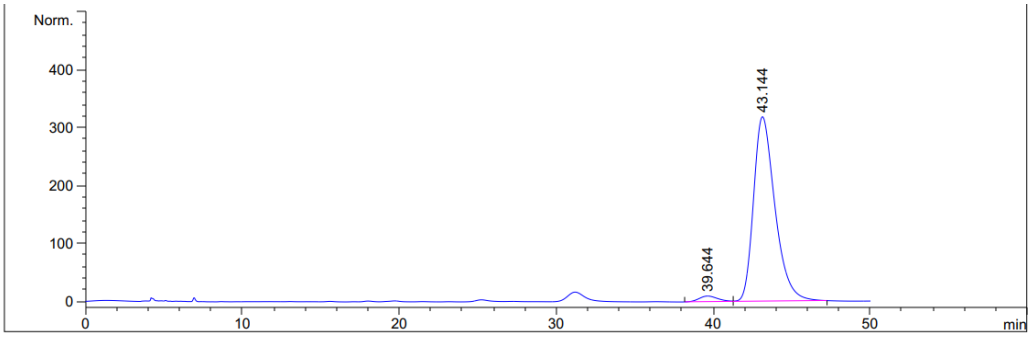
KR-Compound 11a

Prepared according to the procedure within 120 h as yellow solid (32.2 mg, 45% yield, dr > 20:1); mp 115.3-116.3 °C; $[\alpha]_D^{18}$= 45.97 (*c* 0.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.47 (s, 1H), 7.40-7.34 (m, 1H), 7.31-7.24 (m, 4H), 7.22-7.16 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.10-6.99 (m, 5H), 6.98-6.87 (m, 4H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 7.7 Hz, 1H), 5.16 (d, *J* = 8.3 Hz, 1H), 5.00 (d, *J* = 9.0 Hz, 1H), 4.96 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H),

4.42 (t, J = 8.6 Hz, 1H), 3.73 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 176.0, 172.0, 159.6, 151.5, 142.6, 136.8, 135.9, 135.7, 133.1, 132.8, 132.4, 130.2, 130.1, 129.5, 129.3, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.3, 126.7, 124.9, 124.3, 123.2, 118.9, 117.8, 113.9, 108.1, 69.2, 67.3, 66.6, 58.8, 55.2, 49.9, 26.2; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{38}N_2NaO_6^+$ ([M+Na]$^+$) 737.2622, Found 737.2623; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 43.1 min, t_{minor} = 39.6 min).

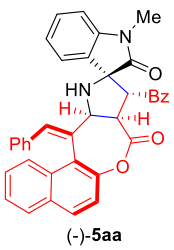


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.467	MM	1.8415	4607.22119	41.69859	50.6954
2	43.500	MM	2.0440	4480.82422	36.53603	49.3046



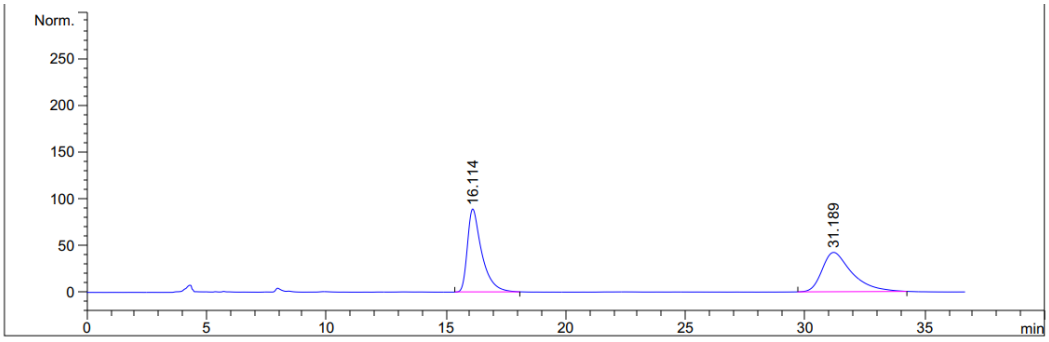
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.644	BV	1.1460	810.93097	9.76956	2.6144
2	43.144	VB	1.4427	3.02075e4	318.11502	97.3856

KR-Compound (–)-5aa

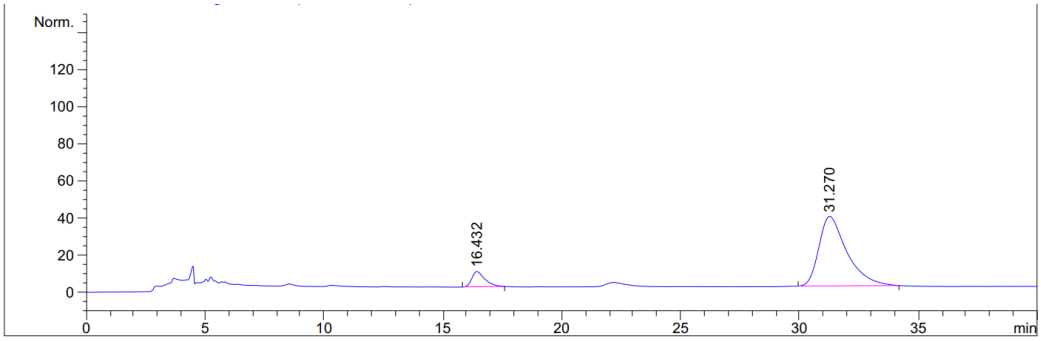


(-)-**5aa**

Prepared according to the procedure within 120 h as white solid (28.8 mg, 50% yield); $[\alpha]_D^{18}$= -85.58 (*c* 0.10, CH_2Cl_2); Enantiomeric excess was determined to be 81% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 31.3 min, t_{minor} = 16.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.114	BB	0.6077	3701.55396	88.69800	50.3819
2	31.189	BB	1.2348	3645.43579	42.02409	49.6181

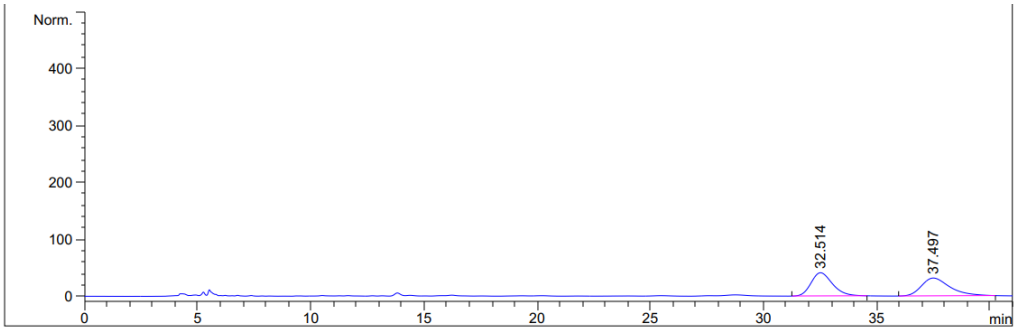


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.432	BB	0.5595	316.08011	8.24217	9.3439
2	31.270	BB	1.1894	3066.65015	37.35004	90.6561

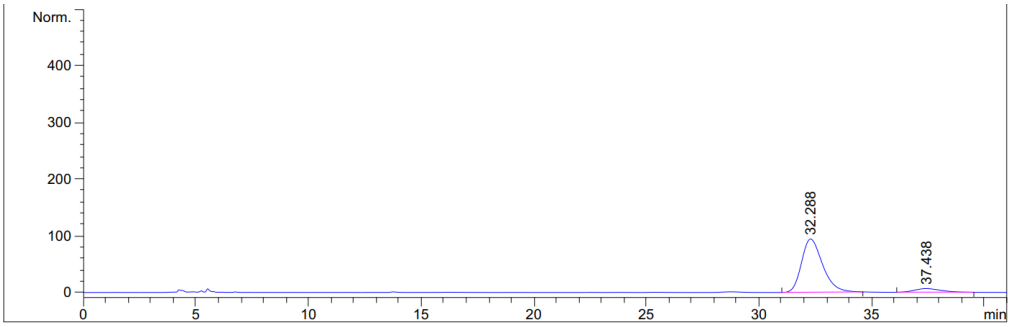
KR-Compound 11b

Prepared according to the procedure within 120 h as white solid (29.3 mg, 41% yield, dr > 20:1); mp 117.4-118.4 °C; $[\alpha]_D^{18}$= 24.55 (*c* 0.11, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.71-7.68 (m, 1H), 7.50 (s, 1H), 7.41-7.37 (m, 1H), 7.32-7.27 (m, 4H), 7.22-7.15 (m, 4H), 7.13-7.09 (m, 1H), 7.07-7.03 (m, 2H), 7.03-6.99 (m, 2H), 6.94-6.90 (m, 3H), 6.81-6.75 (m, 3H), 6.37 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 8.3 Hz, 1H), 5.03 (d, *J* = 9.0 Hz, 1H), 4.99 (d, *J* = 12.5 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.43 (t, *J* = 8.6 Hz, 1H), 3.72 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 176.1, 171.9, 159.7, 151.4, 142.6, 136.7, 136.7, 135.8, 135.7, 133.2, 132.8, 132.4, 130.2, 129.5, 129.3, 128.8, 128.5, 128.4, 128.1, 128.0, 127.8, 127.8, 126.7, 124.9, 124.3, 123.2, 123.2, 120.4, 118.9, 117.6, 114.4, 113.1, 108.1, 69.1, 67.2, 66.5, 58.7, 55.2, 49.8, 26.2; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{38}N_2NaO_6^+$ ($[M+Na]^+$) 737.2622, Found 737.2623; Enantiomeric excess was determined to be 84%

(determined by HPLC using chiral IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 32.3 min, t_{minor} = 37.4 min).

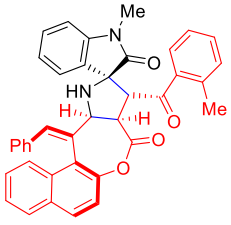


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.514	BB	0.9918	2694.08643	40.79220	49.5111
2	37.497	BB	1.2838	2747.28809	31.32636	50.4889



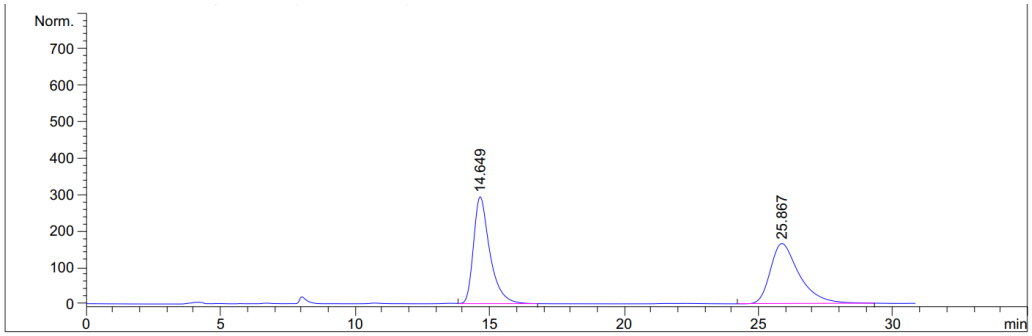
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.288	BB	0.9947	6102.79004	93.82372	92.0295
2	37.438	BB	0.9880	528.55176	6.41158	7.9705

KR-Compound (–)-5ba

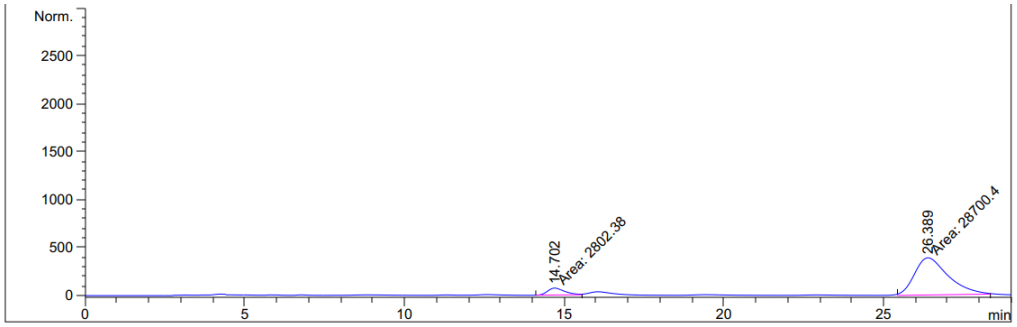


(-)-**5ba**

Prepared according to the procedure within 120 h as white solid (23.6 mg, 40% yield); $[\alpha]_D^{18}$ = -103.61 (*c* 0.53, CH_2Cl_2); Enantiomeric excess was determined to be 83% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 26.4 min, t_{minor} = 14.7 min).



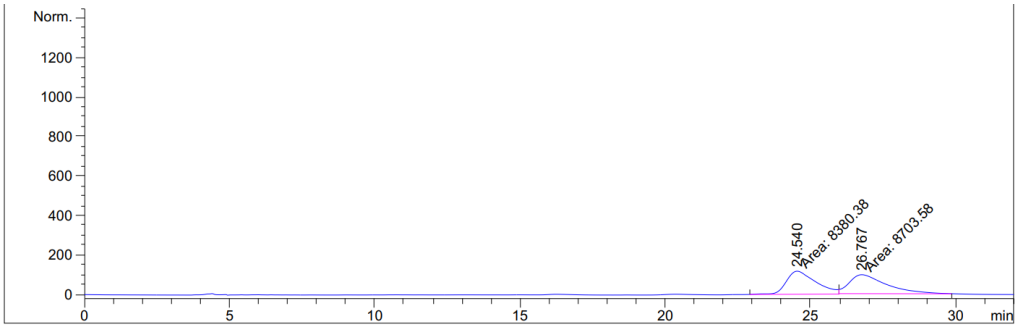
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.649	VB	0.6272	1.24114e4	293.53619	50.1739
2	25.867	VB	1.1200	1.23254e4	165.08441	49.8261



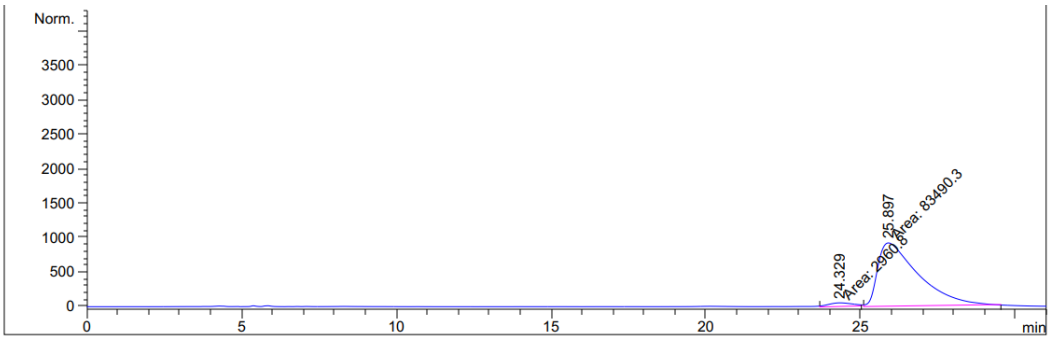
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.702	MM	0.6357	2802.38013	73.47230	8.8957
2	26.389	MM	1.2307	2.87004e4	388.66211	91.1043

KR-Compound 11c

Prepared according to the procedure within 120 h as yellow solid (34.3 mg, 47% yield, dr > 20:1); mp 128.3-129.2 °C; $[\alpha]_D^{18}$= 48.70 (*c* 0.46, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 7.71-7.65 (m, 1H), 7.59 (s, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.27-7.15 (m, 7H), 7.10-6.88 (m, 10H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.44 (t, *J* = 10.0 Hz, 1H), 3.74 (s, 3H), 2.65 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 175.7, 171.9, 159.6, 151.7, 142.9, 138.7, 136.4, 136.0, 135.8, 134.3, 132.2, 131.5, 131.0, 130.2, 130.1, 129.8, 129.3, 129.0, 128.6, 128.4, 128.1, 127.8, 127.2, 126.6, 125.1, 124.7, 124.5, 123.3, 123.1, 119.0, 117.7, 113.8, 108.4, 68.7, 67.3, 65.6, 60.0, 55.2, 49.3, 26.0, 19.5; HRMS (ESI) *m/z* Calcd. for $C_{47}H_{40}N_2NaO_6^+$ ([M+Na]$^+$) 751.2779, Found 751.2777; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 25.9 min, t_{minor} = 24.3 min).

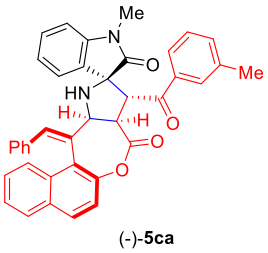


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.540	MM	1.1936	8380.37793	117.01920	49.0541
2	26.767	MM	1.5030	8703.57520	96.51168	50.9459



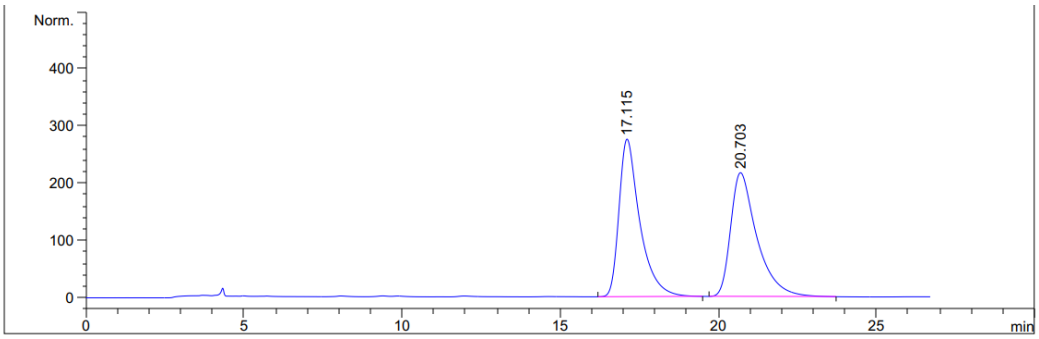
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.329	MM	0.9213	2960.79810	53.56044	3.4248
2	25.897	MM	1.5172	8.34903e4	917.13824	96.5752

KR-Compound (–)-5ca

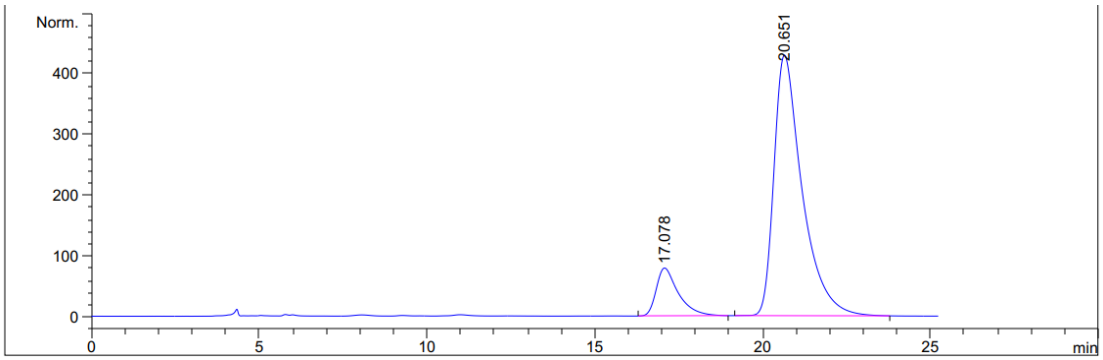


(-)-**5ca**

Prepared according to the procedure within 120 h as white solid (27.2 mg, 46% yield); $[\alpha]_D^{18}$ = -91.62 (*c* 0.57, CH_2Cl_2); Enantiomeric excess was determined to be 75% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 20.7 min, t_{minor} = 17.1 min).



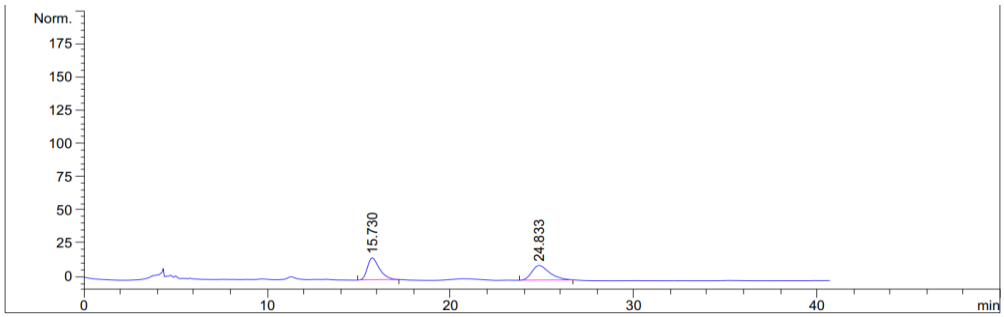
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.115	BB	0.6765	1.25966e4	275.31207	50.2127
2	20.703	BB	0.8569	1.24899e4	216.35785	49.7873



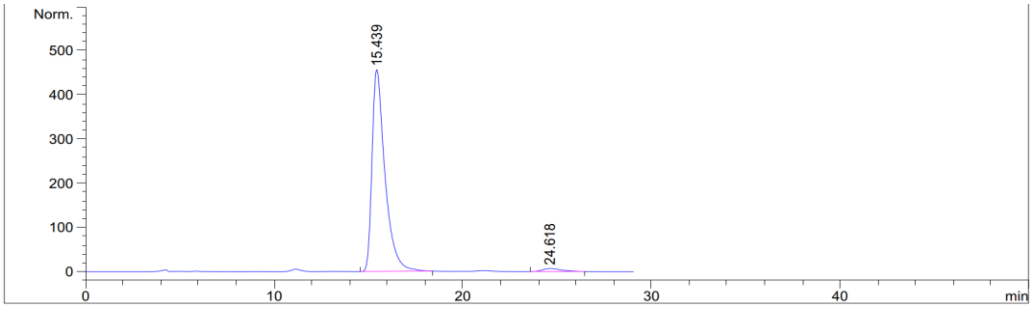
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.078	BB	0.6719	3592.34595	78.75780	12.5621
2	20.651	BB	0.8557	2.50044e4	428.36392	87.4379

KR-Compound 11d

Prepared according to the procedure within 120 h as light yellow solid (32.1 mg, 44% yield, dr > 20:1); mp 127.7-128.6 °C; $[\alpha]_D^{18}$= 49.54 (*c* 0.54, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.65 (m, 3H), 7.48-7.40 (m, 1H), 7.28-6.96 (m, 15H), 6.94-6.85 (m, 3H), 6.75 (d, *J* = 4.1 Hz, 2H), 6.34 (d, *J* = 4.6 Hz, 1H), 5.14 (d, *J* = 4.8 Hz, 1H), 5.04-4.91 (m, 2H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.45-4.33 (m, 1H), 3.73 (s, 3H), 2.84 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 176.2, 172.3, 159.6, 151.4, 142.7, 137.9, 136.9, 135.7, 135.6, 133.5, 133.2, 132.4, 130.2, 129.3, 129.0, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 127.3, 126.7, 125.0, 124.9, 124.3, 123.2, 123.2, 118.9, 117.9, 113.9, 108.0, 69.2, 67.3, 66.7, 59.1, 55.2, 50.0, 26.1, 21.1; HRMS (ESI) *m/z* Calcd. for $C_{47}H_{40}N_2NaO_6^+$ ([M+Na]$^+$) 751.2779, Found 751.2783; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 15.4 min, t_{minor} = 24.6 min).

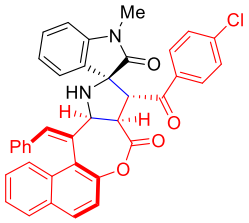


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.730	BB	0.6895	769.15942	16.63080	50.7142
2	24.833	BB	0.9690	747.49695	11.03998	49.2858



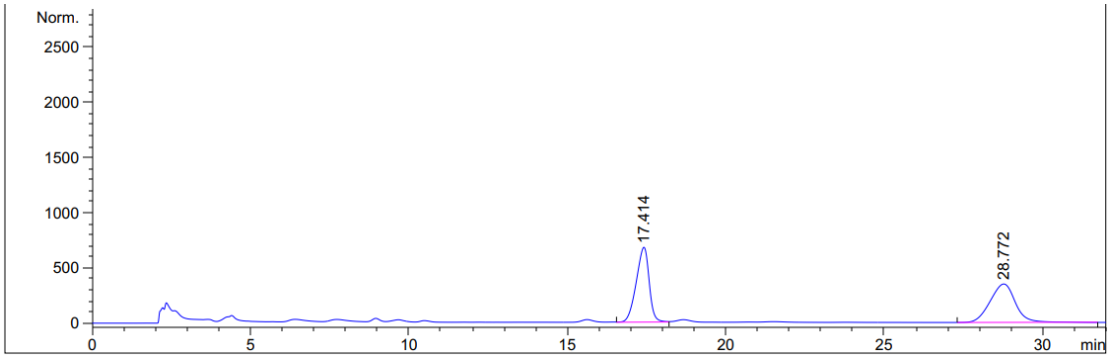
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.439	PB	0.7064	2.17568e4	456.18036	97.7764
2	24.618	BB	0.8318	494.78287	7.15261	2.2236

KR-Compound (–)-5ea

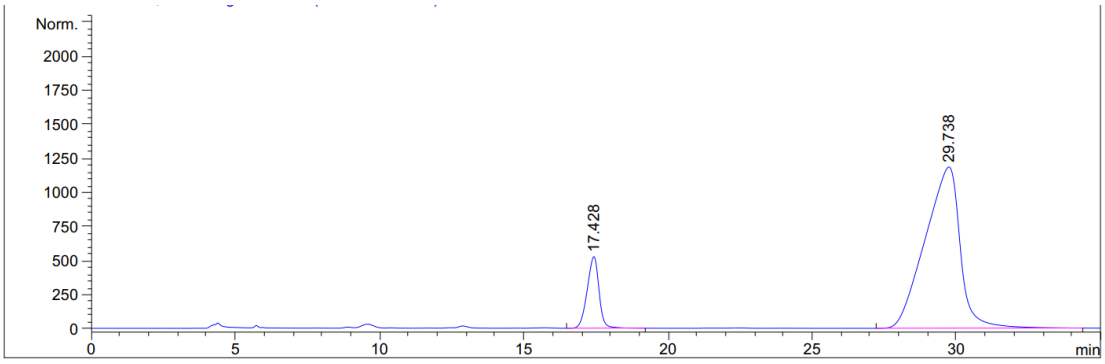


(-)-**5ea**

Prepared according to the procedure within 120 h as white solid (29.3 mg, 48% yield); $[\alpha]_D^{18}$ = -64.10 (*c* 0.61, CH_2Cl_2); Enantiomeric excess was determined to be 74% (determined by HPLC using chiral IA column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 29.7 min, t_{minor} = 17.4 min).



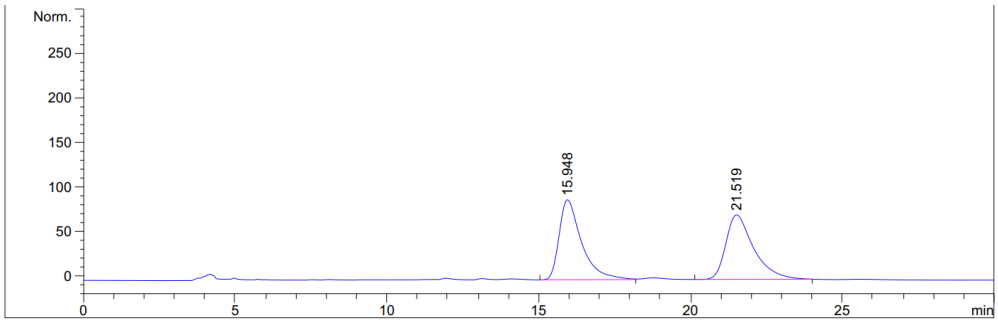
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.414	VV	0.4365	1.93193e4	679.66736	49.7622
2	28.772	BB	0.8542	1.95040e4	349.10599	50.2378



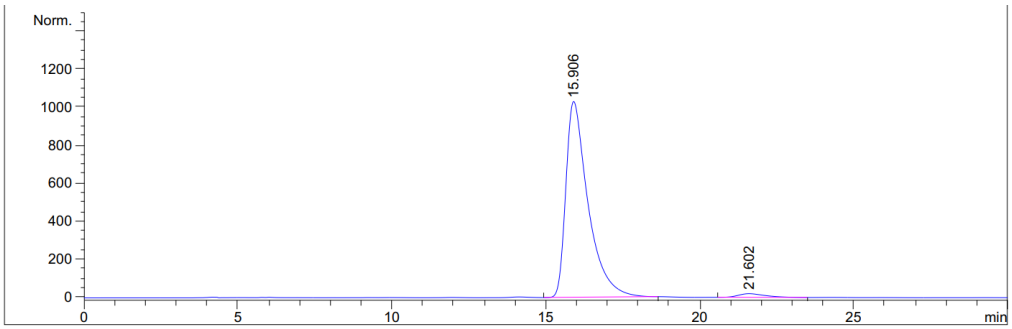
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.428	VB	0.4430	1.49512e4	524.87366	13.0048
2	29.738	PB	1.2152	1.00015e5	1182.66589	86.9952

KR-Compound 11e

Prepared according to the procedure within 120 h as light yellow solid (32.2 mg, 43% yield, dr > 20:1); mp 138.8-139.7 °C; $[\alpha]_D^{18}$= 33.69 (*c* 0.47, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 2H), 7.71-7.64 (m, 1H), 7.45 (s, 1H), 7.30-7.23 (m, 5H), 7.22-7.17 (m, 3H), 7.14-7.09 (m, 3H), 7.07-6.98 (m, 4H), 6.94-6.89 (m, 3H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.93 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.39 (t, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 176.0, 171.8, 159.7, 151.5, 142.5, 139.3, 135.9, 135.6, 135.0, 133.2, 132.3, 130.2, 130.2, 129.6, 129.3, 129.3, 128.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.1, 126.7, 125.0, 124.3, 123.3, 123.2, 118.9, 117.7, 113.8, 108.2, 69.1, 67.3, 66.4, 58.5, 55.2, 50.1, 26.3; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{38}ClN_2O_6^+$ ([M+H]$^+$) 749.2413, Found 749.2417; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 16.0 min, t_{minor} = 21.6 min).

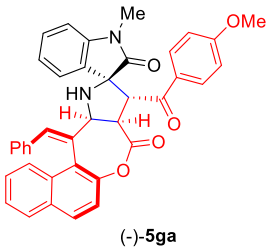


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.948	VB	0.7562	4625.69336	89.66066	50.1160
2	21.519	VB	0.9403	4604.28760	72.22054	49.8840



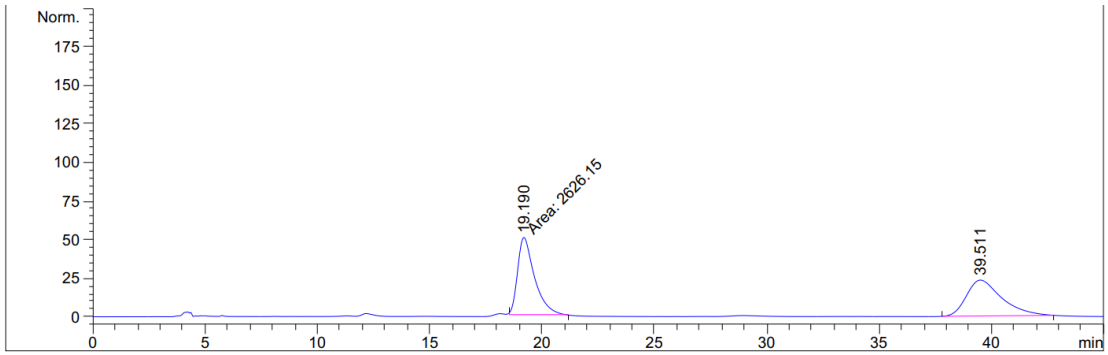
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.906	VB	0.7389	5.17520e4	1030.22009	97.7430
2	21.602	BB	0.8887	1195.00354	19.48572	2.2570

KR-Compound (–)-5ga

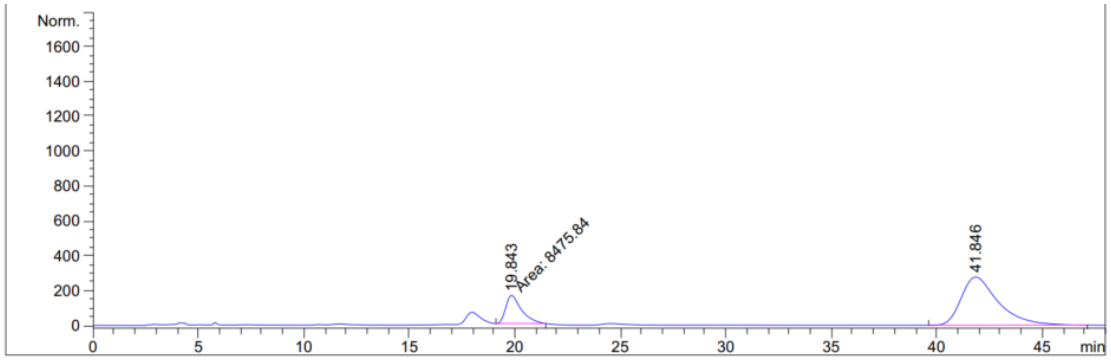


(-)-**5ga**

Prepared according to the procedure within 120 h as white solid (29.1 mg, 48% yield); $[\alpha]_D^{18}$= -48.58 (*c* 0.42, CH_2Cl_2); Enantiomeric excess was determined to be 55% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 41.8 min, t_{minor} = 19.8 min).



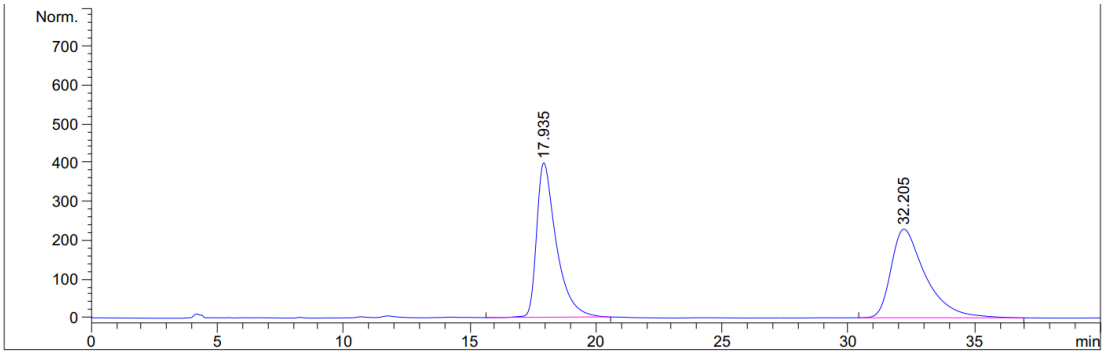
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.190	MM	0.8749	2626.14502	50.02713	50.6493
2	39.511	BB	1.3938	2558.81299	23.29235	49.3507



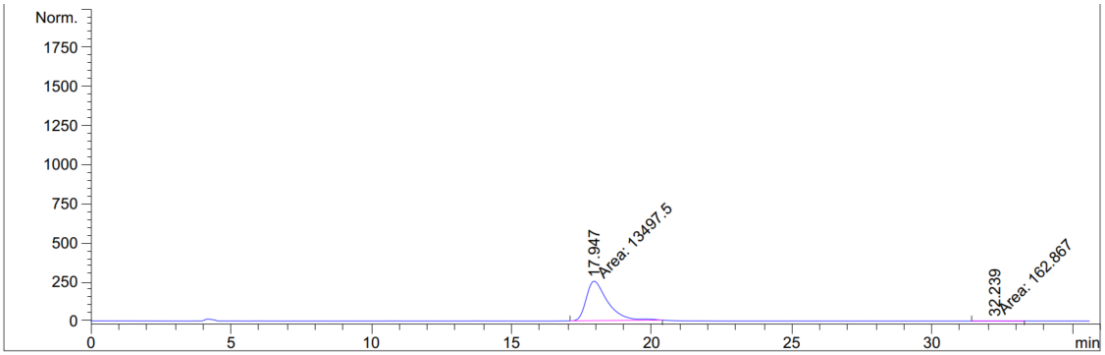
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.843	MM	0.8714	8475.84277	162.10759	20.0251
2	41.846	BB	1.7965	3.38502e4	276.51852	79.9749

KR-Compound 11f

Prepared according to the procedure within 120 h as yellow solid (27.6 mg, 37% yield, dr > 20:1); mp 122.5-123.4 °C; $[\alpha]_D^{18}$= 24.37 (*c* 0.12, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2H), 7.71-7.68 (m, 1H), 7.45 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.30-7.26 (m, 2H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.14-6.98 (m, 8H), 6.93-6.89 (m, 3H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 7.6 Hz, 1H), 5.12 (d, *J* = 8.3 Hz, 1H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.42 (t, *J* = 8.6 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.4, 176.3, 172.2, 163.4, 159.6, 151.4, 142.5, 135.7, 135.7, 133.3, 132.3, 130.3, 130.2, 130.1, 129.6, 129.3, 129.3, 128.9, 128.7, 128.5, 128.4, 128.1, 127.8, 127.2, 126.7, 125.0, 124.3, 123.2, 118.9, 117.9, 113.8, 113.2, 108.0, 69.4, 67.2, 66.6, 58.1, 55.4, 55.2, 50.2, 26.3; HRMS (ESI) *m/z* Calcd. for $C_{47}H_{40}N_2NaO_7^+$ ([M+Na]$^+$) 767.2728, Found 767.2733; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 17.9 min, t_{minor} = 32.3 min).

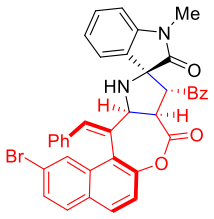


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.935	VB	0.8048	2.16064e4	398.24280	49.9229
2	32.205	BB	1.3864	2.16731e4	228.75539	50.0771



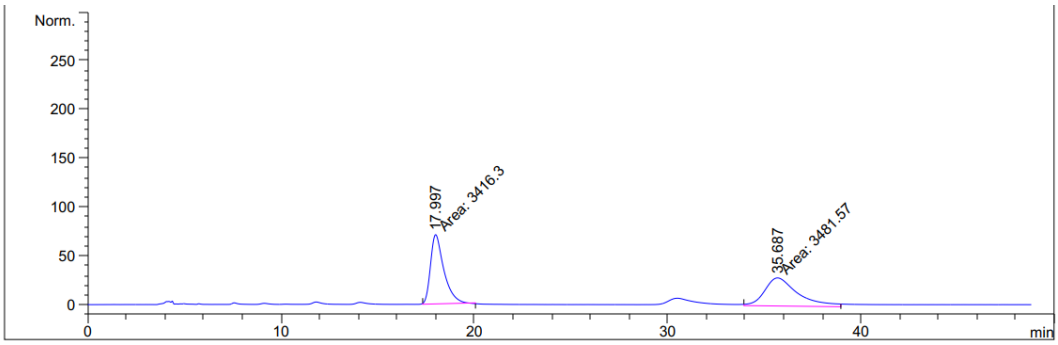
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.947	MM	0.8912	1.34975e4	252.41469	98.8077
2	32.239	MM	0.9383	162.86671	2.04505	1.1923

KR-Compound (–)-5ia

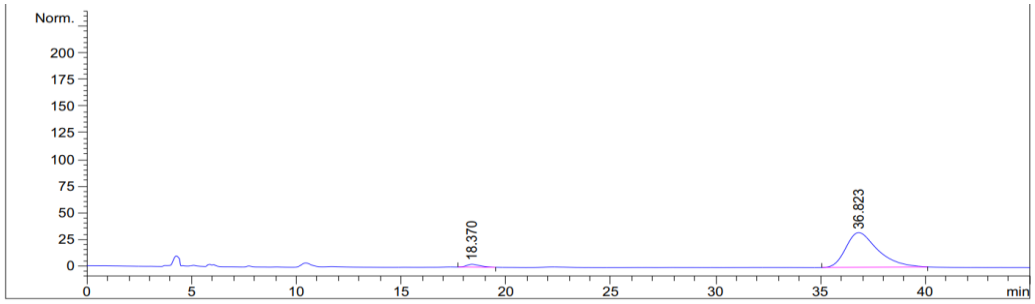


(-)-5ia

Prepared according to the procedure within 120 h as white solid (28.2 mg, 43% yield); $[\alpha]_D^{18}$ = -35.00 (*c* 0.08, CH_2Cl_2); Enantiomeric excess was determined to be 93% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 36.8 min, t_{minor} = 18.4 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.997	MM	0.8025	3416.30371	70.95149	49.5269
2	35.687	MM	2.0146	3481.56934	28.80315	50.4731

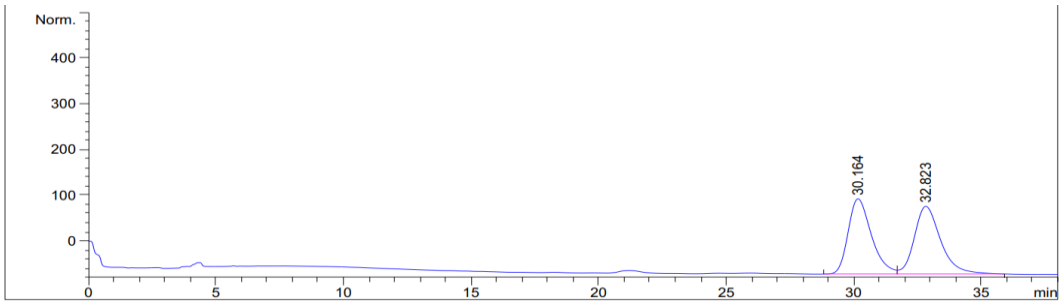


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.370	BB	0.5868	117.43487	2.67311	3.2681
2	36.823	BB	1.5031	3475.93750	32.67674	96.7319

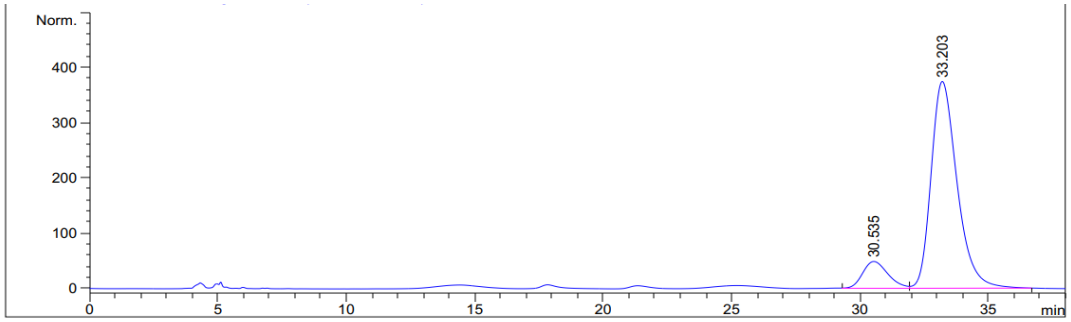
KR-Compound 11g

Prepared according to the procedure within 120 h as light yellow solid (34.9 mg, 44% yield, dr > 20:1); mp 130.2-131.2 °C; $[\alpha]_D^{18}$= 17.07 (*c* 0.33, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.86-7.83 (m, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.41 (s, 1H), 7.40-7.36 (m, 1H), 7.33-7.29 (m, 3H), 7.24-7.19 (m, 3H), 7.14-7.09 (m,

4H), 7.06-6.95 (m, 5H), 6.89 (d, *J* = 7.3 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 7.7 Hz, 1H), 5.16 (d, *J* = 8.3 Hz, 1H), 5.02 (d, *J* = 9.0 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.38 (t, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 176.0, 171.6, 159.6, 153.0, 142.6, 136.7, 136.4, 135.6, 133.7, 132.8, 132.3, 130.6, 130.1, 130.1, 129.9, 129.6, 128.6, 128.5, 128.1, 128.0, 127.9, 127.6, 127.3, 126.7, 126.4, 124.8, 123.4, 121.1, 119.6, 116.7, 113.9, 108.1, 68.9, 67.1, 66.2, 58.3, 55.2, 49.3, 26.2; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{37}BrN_2NaO_6^+$ ([M+Na]$^+$) 815.1727, Found 815.1726; Enantiomeric excess was determined to be 77% (determined by HPLC using chiral IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 ºC, 0.8 mL/min, t_{major} = 33.2 min, t_{minor} = 30.5 min).

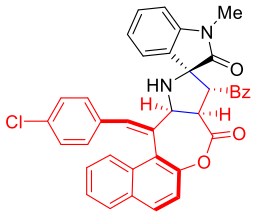


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.164	BV	0.9601	1.04207e4	164.22964	49.5924
2	32.823	VB	1.0712	1.05920e4	147.66824	50.4076



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.535	BV	1.0309	3348.36426	48.78033	11.2902
2	33.203	VB	1.0573	2.63090e4	374.34518	88.7098

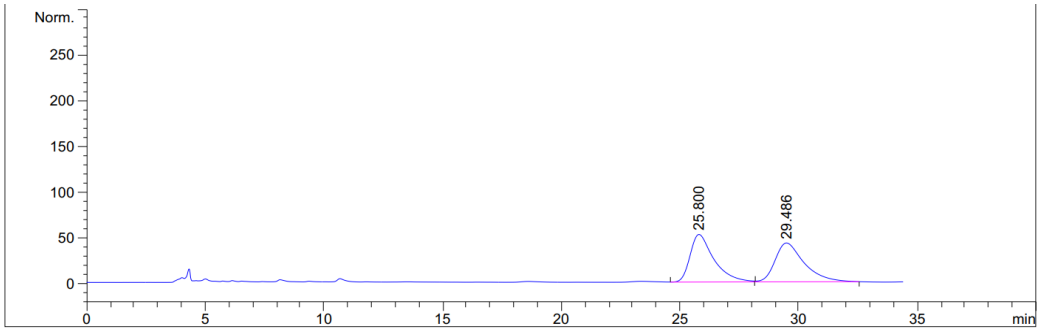
KR-Compound (–)-5ka



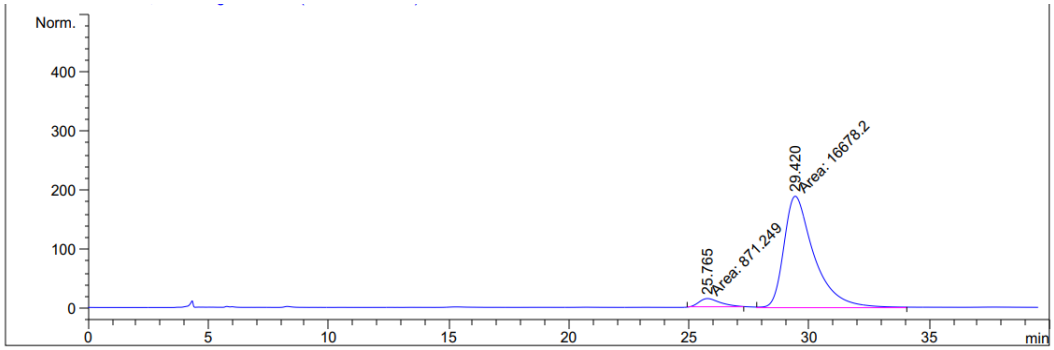
(-)-**5ka**

Prepared according to the procedure within 120 h as white solid (25.7 mg, 42% yield); $[\alpha]_D^{18}$ = -106.32 (*c* 0.57, CH_2Cl_2); Enantiomeric excess was determined to be 90% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ

= 254 nm, 30 °C, 0.8 mL/min, t_{major} = 29.4 min, t_{minor} = 25.8 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.800	VB	1.0196	3629.78955	51.90930	50.0087
2	29.486	BB	1.2561	3628.52197	42.46320	49.9913

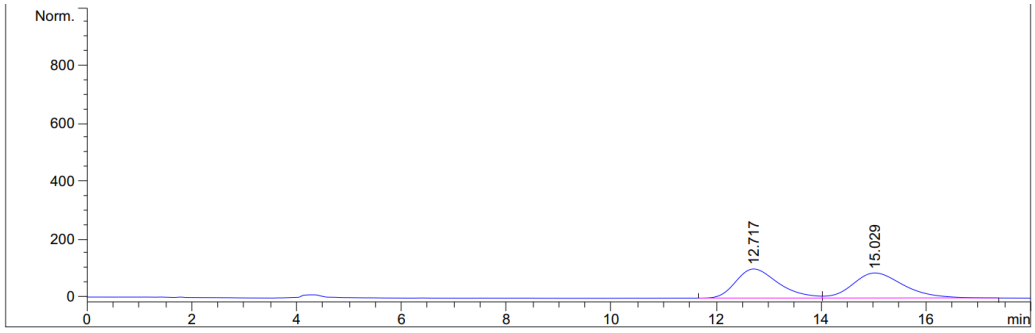


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.765	MM	1.0331	871.24921	14.05536	4.9645
2	29.420	MM	1.4678	1.66782e4	189.37865	95.0355

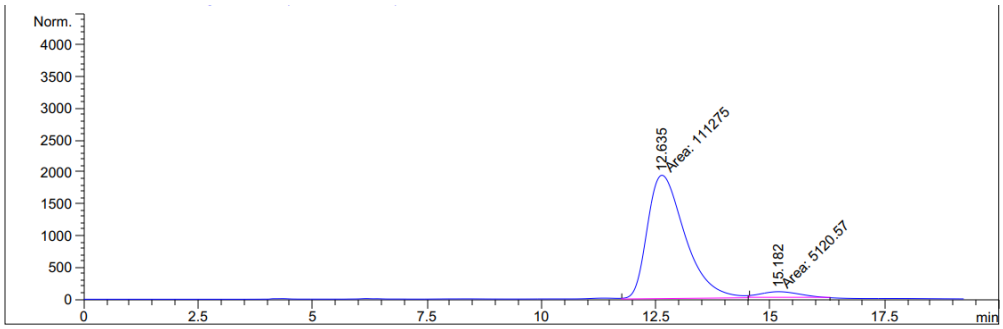
KR-Compound 11h

Prepared according to the procedure within 120 h as white solid (33.7 mg, 45% yield, dr > 20:1); mp 132.1-132.9 °C; $[\alpha]_D^{18}$= 22.80 (*c* 0.25, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.66-7.63 (m, 1H), 7.40-7.36 (m, 2H), 7.31-7.26 (m, 4H), 7.22-7.18 (m, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.10-7.06 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.91-6.88 (m, 1H), 6.82-6.79 (m, 2H), 6.75-6.72 (m, 2H), 6.35 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 8.4 Hz, 1H), 4.97 (t, *J* = 11.2 Hz, 2H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.41 (t, *J* = 8.6 Hz, 1H), 3.73 (s, 3H), 2.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 176.3, 172.1, 159.7, 151.5, 142.6, 136.7, 134.5, 134.3, 134.1, 133.4, 132.8, 132.2, 130.4, 130.2, 129.7, 129.5, 129.3, 128.8, 128.5, 128.3, 128.0, 127.8, 127.2, 126.8, 124.8, 124.1, 123.3, 123.2, 119.0, 117.5, 113.9, 108.1, 69.1, 67.4, 66.3, 58.6, 55.2, 50.0, 26.2; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{37}ClN_2NaO_6^+$ ($[M+Na]^+$) 771.2232, Found 771.2231; Enantiomeric excess was determined to be 91%

(determined by HPLC using chiral OD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.6 min, t_{minor} = 15.2 min).

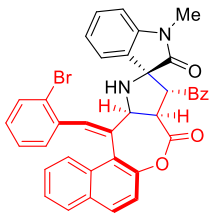


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.717	PV	0.8690	5701.83447	100.66525	49.2876
2	15.029	VB	1.0246	5866.66113	86.77345	50.7124



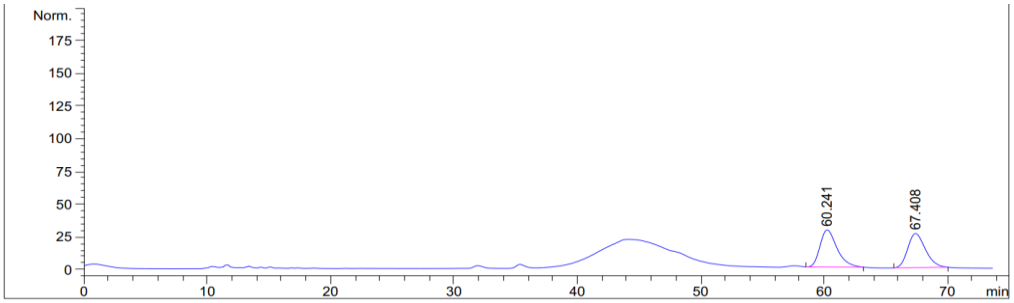
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.635	MM	0.9554	1.11275e5	1941.23645	95.6007
2	15.182	MM	0.9647	5120.57080	88.46569	4.3993

KR-Compound (–)-5la

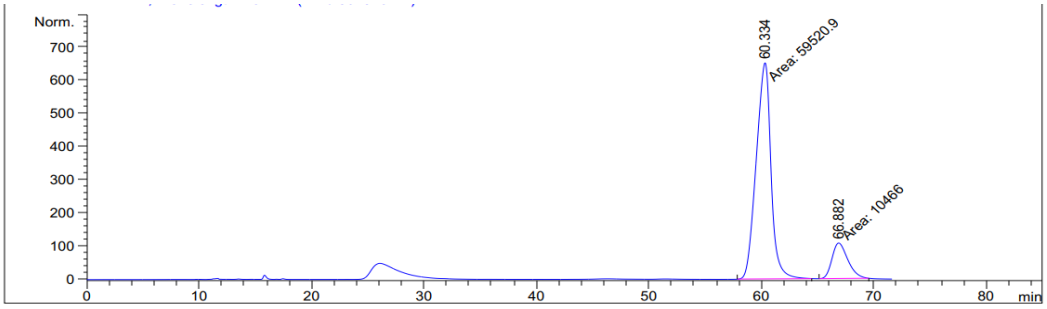


(-)-**5la**

Prepared according to the procedure within 120 h as white solid (30.1 mg, 46% yield); $[\alpha]_D^{18}$ = -173.51 (*c* 0.42, CH_2Cl_2); Enantiomeric excess was determined to be 71% (determined by HPLC using chiral AD-H+IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 66.9 min, t_{minor} = 60.3 min).



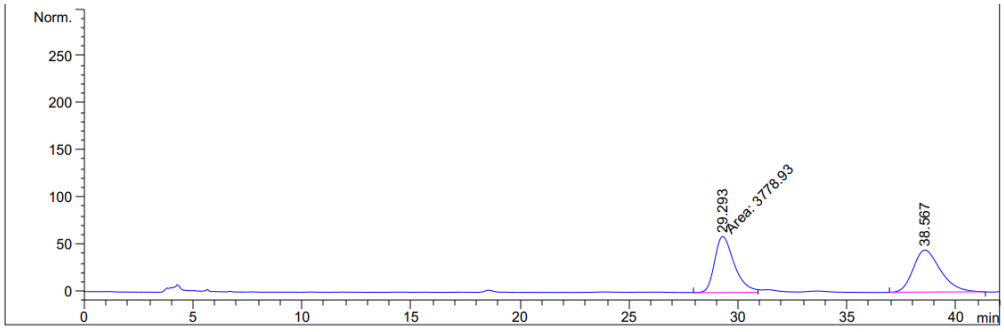
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.241	VB	1.3474	2750.09155	28.45477	51.3647
2	67.408	BB	1.3979	2603.95459	26.04449	48.6353



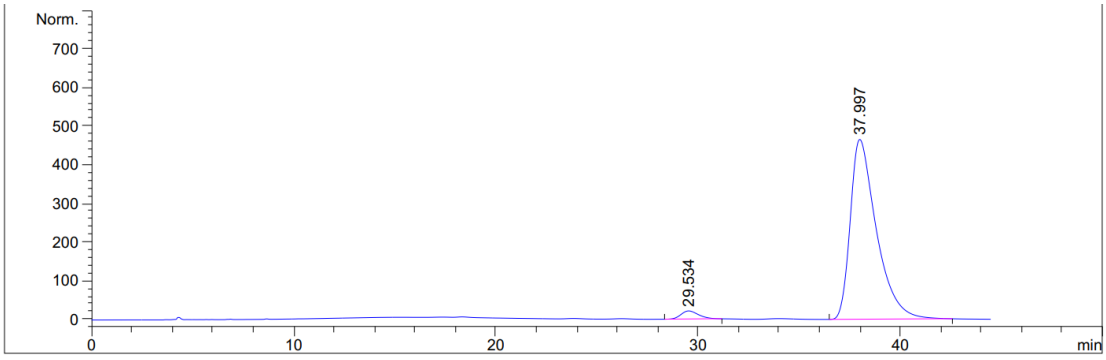
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	60.334	MM	1.5235	5.95209e4	651.15576	85.0457
2	66.882	MM	1.6304	1.04660e4	106.98863	14.9543

KR-Compound 11i

Prepared according to the procedure within 120 h as white solid (33.3 mg, 42% yield, dr > 20:1); mp 136.4-137.2 °C; $[\alpha]_D^{18}$= 80.29 (*c* 0.49, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.74-7.65 (m, 4H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.42-7.38 (m, 1H), 7.36-7.28 (m, 3H), 7.26-7.21 (m, 3H), 7.17-7.11 (m, 3H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.98-6.93 (m, 1H), 6.90-6.83 (m, 1H), 6.73-6.64 (m, 4H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.24 (d, *J* = 9.2 Hz, 1H), 5.11 (d, *J* = 9.5 Hz, 1H), 4.84 (d, *J* = 12.0 Hz, 1H), 4.50 (dd, *J* = 16.0, 6.9 Hz, 2H), 3.72 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 175.9, 171.6, 159.5, 152.3, 142.5, 136.8, 136.5, 136.5, 136.2, 132.8, 132.5, 132.1, 130.2, 130.0, 129.6, 129.5, 129.0, 129.0, 128.7, 128.3, 128.1, 127.9, 127.3, 126.7, 126.6, 124.9, 124.4, 123.9, 123.2, 123.0, 118.9, 116.6, 113.7, 108.1, 69.1, 67.2, 65.5, 58.3, 55.2, 49.6, 26.1; HRMS (ESI) *m/z* Calcd. for $C_{46}H_{37}BrN_2NaO_6^+$ ($[M+Na]^+$) 815.1727, Found 815.1725; Enantiomeric excess was determined to be 94% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 38.0 min, t_{minor} = 29.5 min).

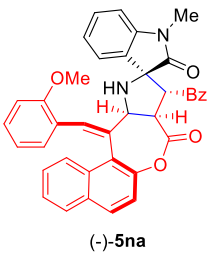


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.293	MM	1.0550	3778.92896	59.69654	49.0589
2	38.567	BB	1.2875	3923.91089	44.70668	50.9411



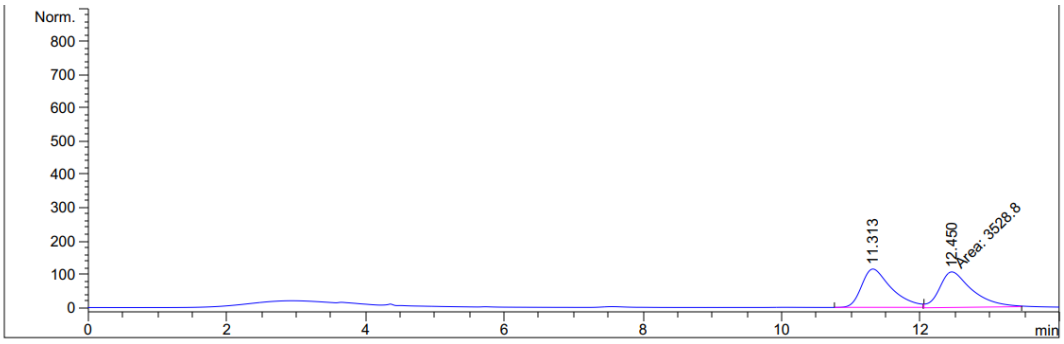
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.534	BB	0.8975	1276.19482	21.02283	2.9651
2	37.997	BB	1.3160	4.17645e4	464.88159	97.0349

KR-Compound (–)-5na

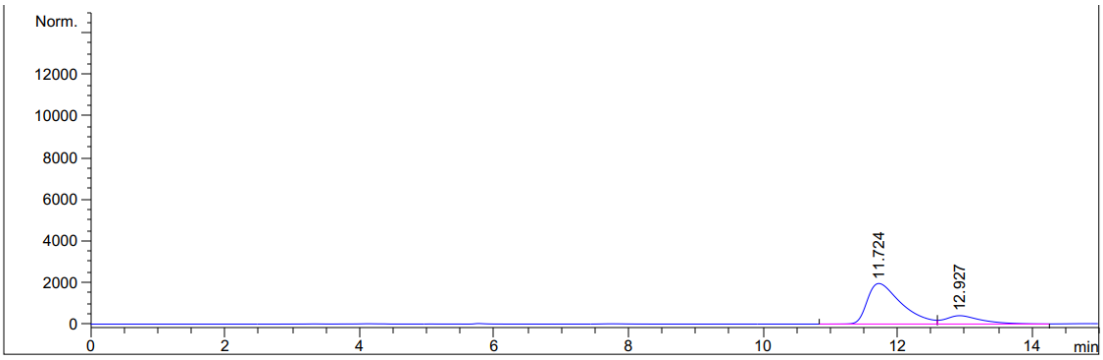


(-)-**5na**

Prepared according to the procedure within 120 h as white solid (31.5 mg, 52% yield); $[\alpha]_D^{18}$ = -141.36 (*c* 0.46, CH_2Cl_2); Enantiomeric excess was determined to be 63% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 11.7 min, t_{minor} = 12.9 min).



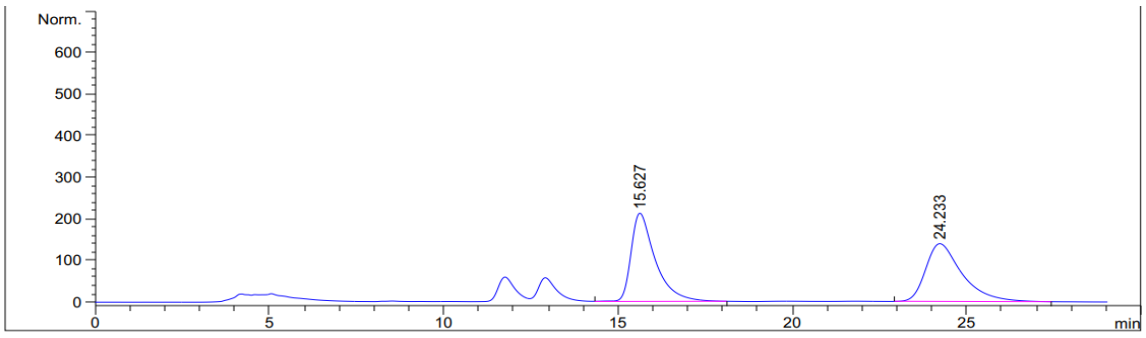
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.313	MM	0.5068	3520.32349	115.76198	49.1294
2	12.450	MM	0.5690	3645.08228	106.77081	50.8706



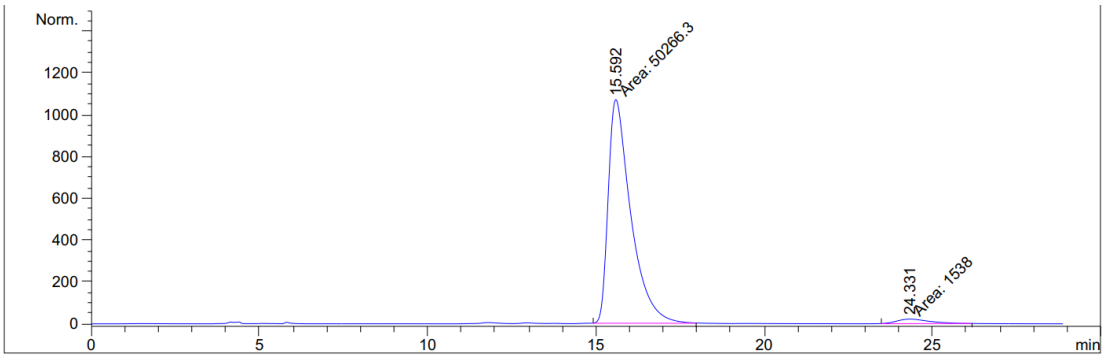
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.724	VV	0.5249	6.87545e4	1949.87549	81.8525
2	12.927	VV	0.5437	1.52435e4	403.89236	18.1475

KR-Compound 11j

Prepared according to the procedure within 120 h as white solid (28.3 mg, 38% yield, dr > 20:1); mp 120.5-121.4 °C; $[\alpha]_D^{18}$= 62.45 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.70 (m, 2H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.61 (s, 1H), 7.41-7.34 (m, 1H), 7.32-7.26 (m, 3H), 7.25-7.05 (m, 9H), 7.04-6.98 (m, 1H), 6.95-6.88 (m, 1H), 6.76 (d, *J* = 8.6 Hz, 3H), 6.62-6.56 (m, 1H), 6.42-6.34 (m, 2H), 5.17 (d, *J* = 7.9 Hz, 1H), 5.04 (d, *J* = 9.2 Hz, 1H), 4.90 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.47-4.39 (m, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 175.6, 171.9, 159.5, 156.9, 151.9, 142.6, 136.8, 133.2, 132.7, 132.6, 131.4, 130.0, 129.9, 129.4, 129.1, 129.0, 128.7, 128.6, 128.3, 128.0, 127.9, 127.4, 126.4, 125.1, 125.0, 124.6, 123.1, 122.9, 120.1, 118.9, 117.6, 113.8, 110.1, 108.1, 69.3, 67.1, 66.9, 59.0, 55.5, 55.2, 49.5, 26.1; HRMS (ESI) *m/z* Calcd. for $C_{47}H_{40}N_2NaO_7^+$ ([M+Na]$^+$) 767.2728, Found 767.2729; Enantiomeric excess was determined to be 94% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 15.6 min, t_{minor} = 24.3 min).

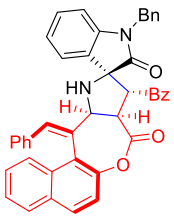


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.627	BB	0.7128	1.02136e4	211.72586	50.3536
2	24.233	BB	1.0673	1.00702e4	138.87512	49.6464



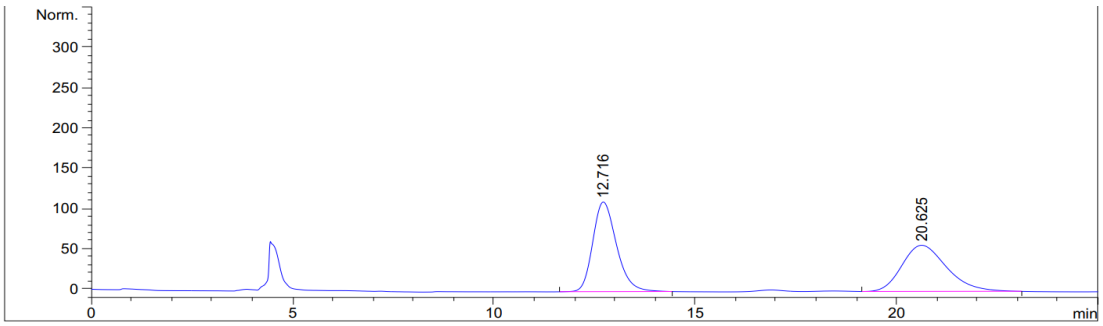
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.592	MM	0.7827	5.02663e4	1070.40088	97.0311
2	24.331	MM	1.1504	1538.00488	22.28256	2.9689

KR-Compound (–)-5ac

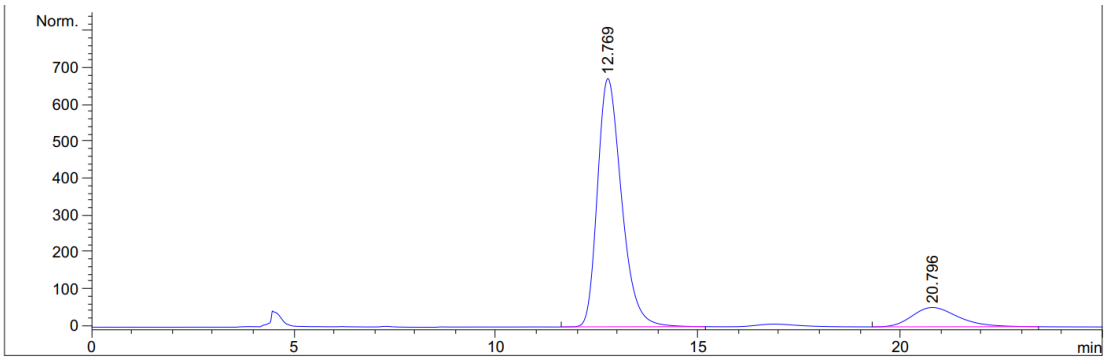


(-)-**5ac**

Prepared according to the procedure within 120 h as white solid (28.7 mg, 44% yield); $[\alpha]_D^{18}$= -78.48 (*c* 0.45, CH_2Cl_2); Enantiomeric excess was determined to be 74% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 12.8 min, t_{minor} = 20.8 min).



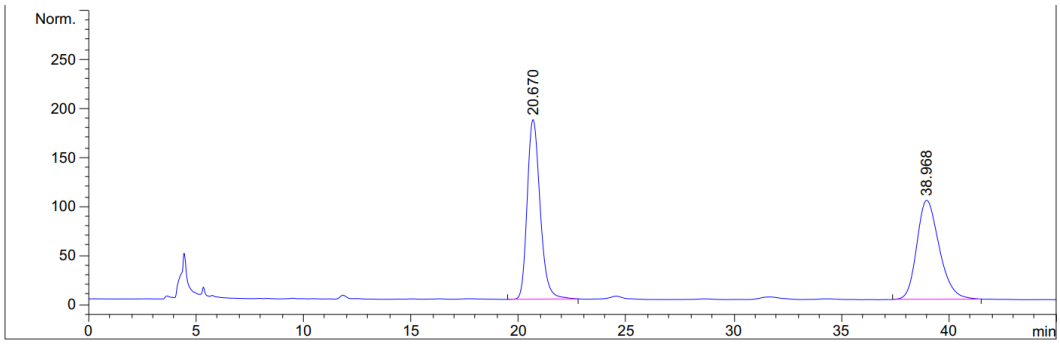
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.716	BB	0.6275	4581.56982	111.25667	50.7030
2	20.625	VB	1.1759	4454.53125	57.42118	49.2970



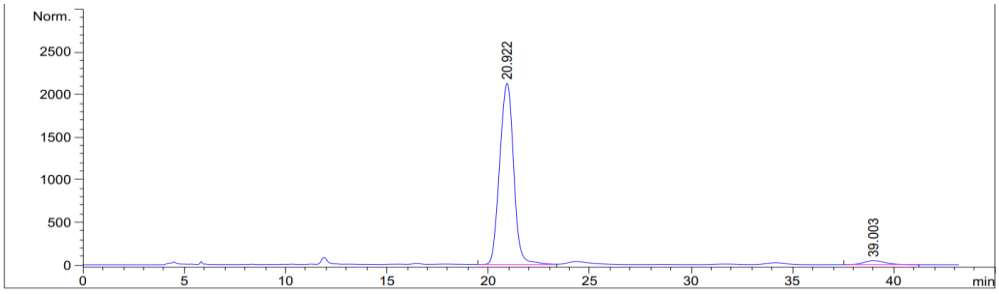
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.769	BB	0.6384	2.79395e4	673.33539	87.0216
2	20.796	BB	1.2128	4166.87744	52.41623	12.9784

KR-Compound 11k

Prepared according to the procedure within 120 h as light yellow solid (33.2 mg, 42% yield, dr > 20:1); mp 129.0-130.0 °C; $[\alpha]_D^{18}$= 48.71 (*c* 0.43, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.80-7.68 (m, 3H), 7.50-7.40 (m, 4H), 7.31-7.26 (m, 2H), 7.24-7.17 (m, 6H), 7.13-7.06 (m, 3H), 7.06-6.96 (m, 6H), 6.96-6.85 (m, 3H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.33 (d, *J* = 7.8 Hz, 1H), 5.28 (d, *J* = 8.6 Hz, 1H), 5.03 (d, *J* = 8.7 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.46 (t, *J* = 8.8 Hz, 1H), 4.31 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 3.14 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 176.3, 171.9, 159.6, 151.6, 141.9, 136.6, 135.8, 135.7, 135.0, 133.3, 133.1, 132.3, 130.2, 130.2, 129.4, 129.3, 128.8, 128.8, 128.6, 128.4, 128.3, 128.1, 127.8, 127.7, 127.3, 127.2, 126.7, 125.2, 124.4, 123.2, 123.2, 119.0, 117.7, 113.8, 109.3, 69.2, 67.2, 66.3, 57.6, 55.2, 50.4, 44.3; HRMS (ESI) *m/z* Calcd. for $C_{52}H_{43}N_2O_6^+$ ($[M+H]^+$) 791.3116, Found 791.3116; Enantiomeric excess was determined to be 93% (determined by HPLC using chiral IA column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 21.0 min, t_{minor} = 39.0 min).

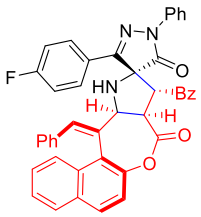


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.670	BB	0.6430	7658.65430	183.38397	51.0088
2	38.968	BB	1.0719	7355.71875	101.23952	48.9912



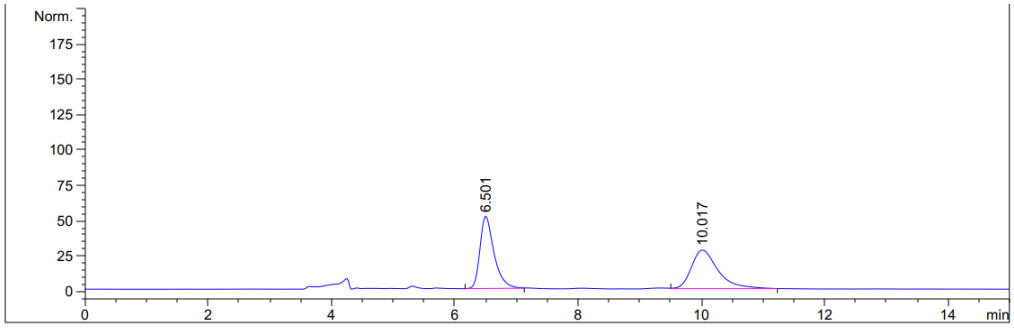
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.922	VV	0.7590	1.02128e5	2124.00830	96.7468
2	39.003	BB	1.0744	3434.16846	46.64688	3.2532

KR-Compound (–)-3ab

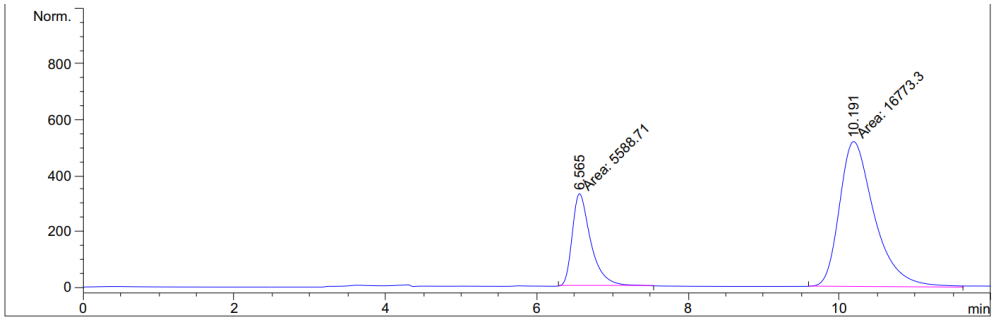


(-)-**3ab**

Prepared according to the procedure within 168 h as white solid (34.2 mg, 50% yield); $[\alpha]_D^{18}$= -10.53 (*c* 0.49, CH_2Cl_2); Enantiomeric excess was determined to be 50% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.2 min, t_{minor} = 6.6 min).



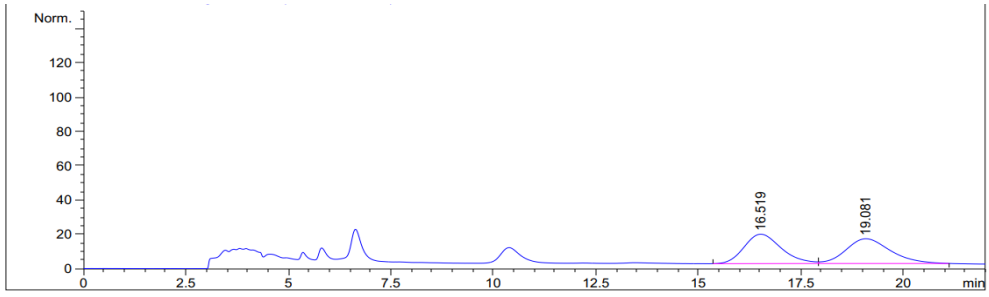
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.501	BB	0.2379	809.97375	50.93932	49.4591
2	10.017	VB	0.4520	827.69098	27.35371	50.5409



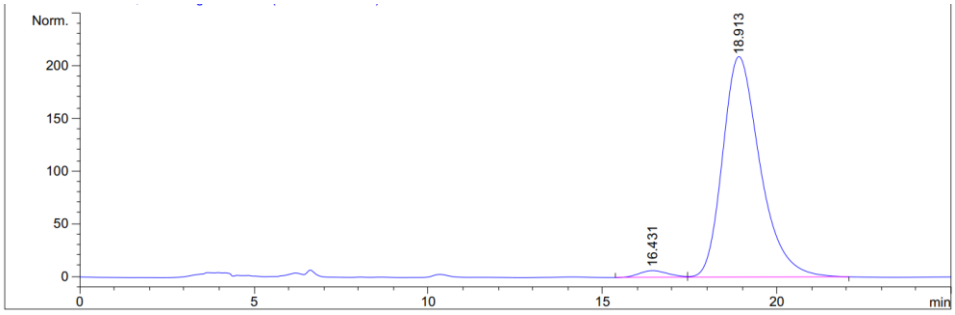
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.565	MM	0.2827	5588.71338	329.49185	24.9920
2	10.191	MM	0.5376	1.67733e4	520.01520	75.0080

KR-Compound 12a

Prepared according to the procedure within 168 h as white solid (26.3 mg, 32% yield, dr > 20:1); mp 125.6-126.6 °C; $[\alpha]_D^{18}$= -27.44 (*c* 0.27, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44-8.39 (m, 2H), 7.78-7.73 (m, 2H), 7.62 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.42-7.37 (m, 2H), 7.35-7.29 (m, 4H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 3H), 7.16-7.05 (m, 8H), 6.98-6.95 (m, 2H), 6.73-6.70 (m, 2H), 5.40 (d, *J* = 9.5 Hz, 1H), 5.20-5.03 (m, 2H), 4.88 (d, *J* = 11.8 Hz, 1H), 4.48 (dd, *J* = 9.4, 7.5 Hz, 1H), 3.76 (s, 3H), 2.92 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.6, 173.4, 173.3, 164.3 (d, *J* = 252.2 Hz), 160.0, 154.1, 151.2, 137.3, 136.5, 136.1, 135.4, 133.4, 131.7, 130.7, 130.2, 129.5, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 126.9, 126.4, 125.4, 123.4, 123.3, 119.0, 118.8, 118.6, 116.0 (d, *J* = 21.1 Hz), 114.0, 71.5, 68.2, 63.1, 56.6, 55.2, 48.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.26; HRMS (ESI) *m/z* Calcd. for $C_{52}H_{41}FN_3O_6^+$ ($[M+H]^+$) 822.2974, Found 822.2982; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 18.9 min, t_{minor} = 16.4 min).

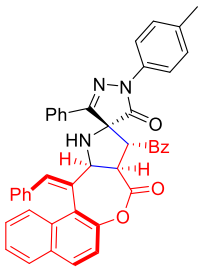


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.519	BV	0.9067	1091.21765	17.18755	49.7444
2	19.081	VB	1.0181	1102.43079	14.49978	50.2556



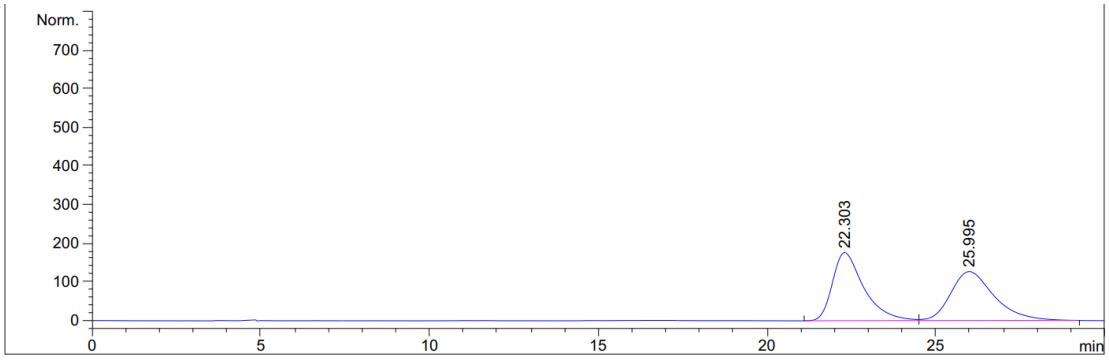
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.431	PV	0.7854	381.01056	6.46258	2.3674
2	18.913	VB	1.1511	1.57133e4	209.63759	97.6326

KR-Compound (–)-3ah

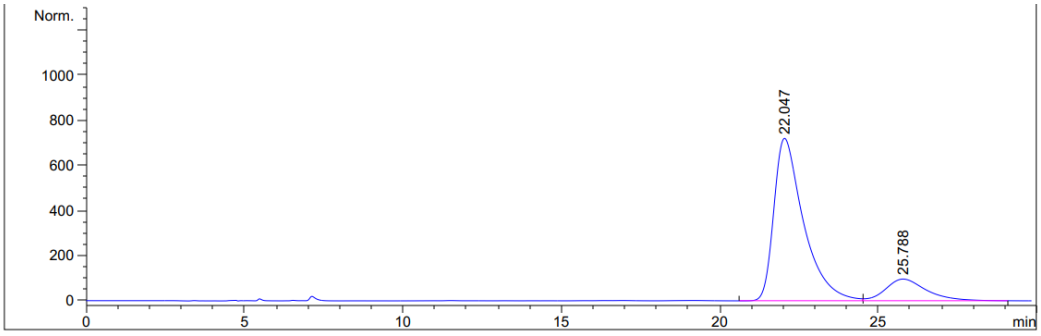


(-)-3ah

Prepared according to the procedure within 168 h as white solid (31.9 mg, 47% yield); $[\alpha]_D^{18}$= -7.97 (*c* 0.83, CH_2Cl_2); Enantiomeric excess was determined to be 69% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 80/20, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 22.0 min, t_{minor} = 25.8 min).



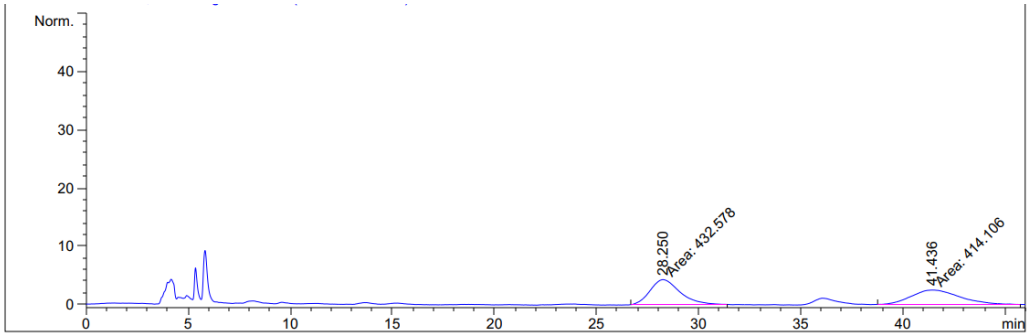
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.303	BB	0.9610	1.14201e4	176.30986	50.0598
2	25.995	BB	1.3348	1.13928e4	126.83072	49.9402



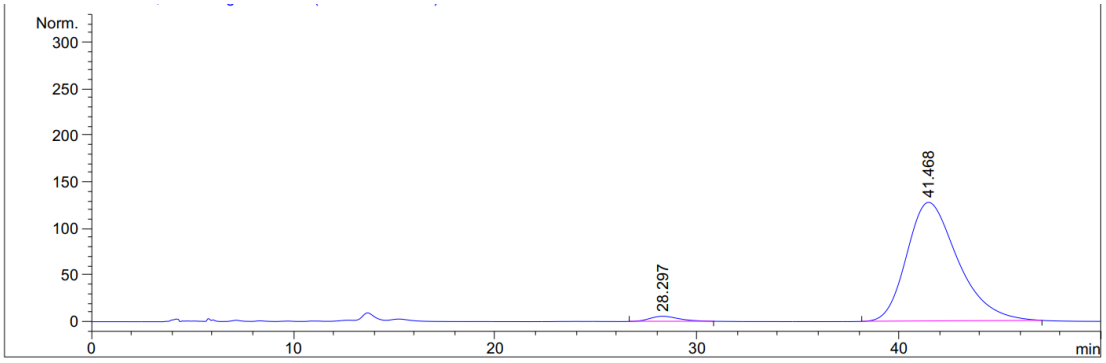
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.047	VV	0.9648	4.70223e4	720.89783	84.5365
2	25.788	VB	1.3093	8601.33594	96.36187	15.4635

KR-Compound 12b

Prepared according to the procedure within 168 h as white solid (31.9 mg, 39% yield, dr > 20:1); mp 137.3-138.0 °C; $[\alpha]_D^{18}$= -44.03 (*c* 0.56, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 8.46-8.40 (m, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.60-7.53 (m, 3H), 7.52-7.49 (m, 2H), 7.42-7.38 (m, 2H), 7.37-7.34 (m, 2H), 7.31-7.26 (m, 2H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.15-7.04 (m, 9H), 7.01-6.97 (m, 2H), 6.72-6.67 (m, 2H), 5.39 (d, *J* = 9.5 Hz, 1H), 5.20 (d, *J* = 7.8 Hz, 1H), 5.10 (d, *J* = 11.8 Hz, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.56 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.75 (s, 3H), 2.93 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 173.4, 173.3, 159.8, 154.9, 151.3, 136.6, 136.1, 135.6, 135.1, 134.9, 133.8, 133.4, 131.8, 130.8, 130.6, 130.3, 130.1, 129.3, 129.2, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.3, 126.9, 126.5, 123.6, 123.3, 119.1, 118.8, 118.8, 113.9, 71.7, 68.0, 63.1, 56.3, 55.2, 48.5, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{53}H_{44}N_3O_6^+$ ($[M+H]^+$) 818.3225, Found 818.3220; Enantiomeric excess was determined to be 95% (determined by HPLC using chiral IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 41.5 min, t_{minor} = 28.3 min).

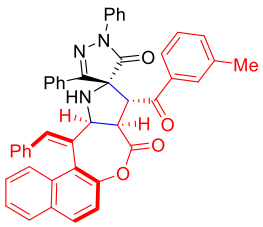


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.250	MM	1.7000	439.84677	4.31213	50.9023
2	41.436	MM	2.8093	424.25244	2.51692	49.0977



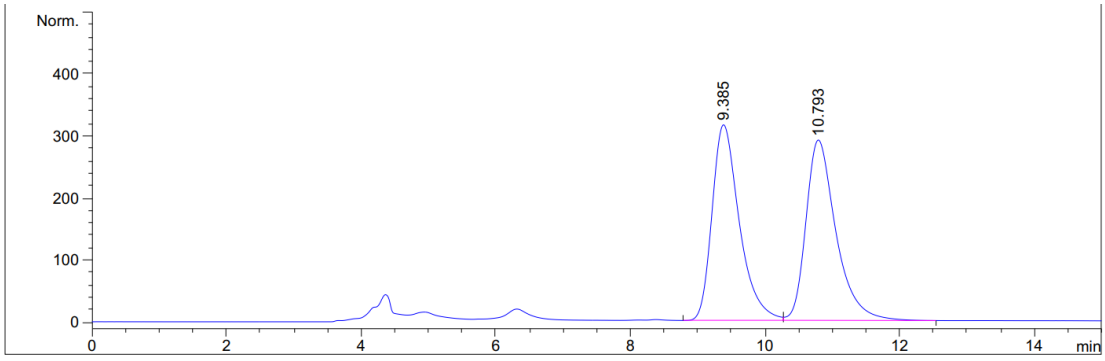
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.297	BB	1.1908	560.89246	5.54289	2.4337
2	41.468	BB	2.4611	2.24861e4	127.57444	97.5663

KR-Compound (–)-3ca

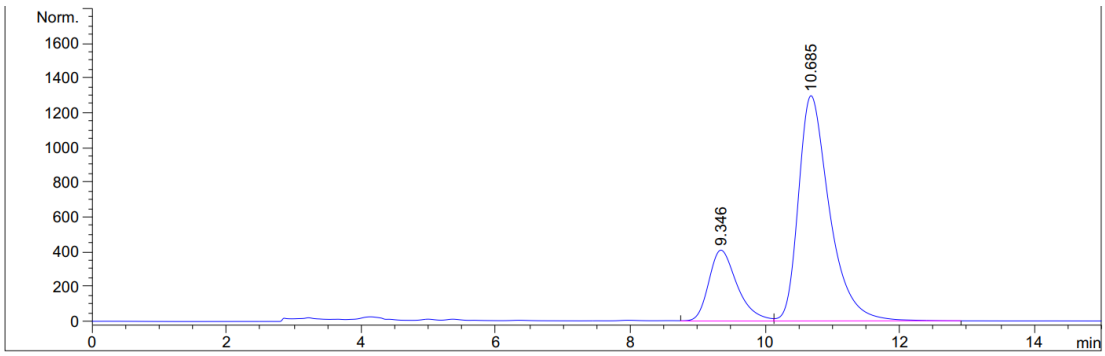


(-)-**3ca**

Prepared according to the procedure within 168 h as white solid (31.9 mg, 47% yield); $[\alpha]_D^{18}$ = -14.36 (*c* 0.37, CH_2Cl_2); Enantiomeric excess was determined to be 55% (determined by HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 10.7 min, t_{minor} = 9.3 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.385	VV	0.4270	8910.99512	315.57254	49.6116
2	10.793	VB	0.4675	9050.53809	291.12088	50.3884

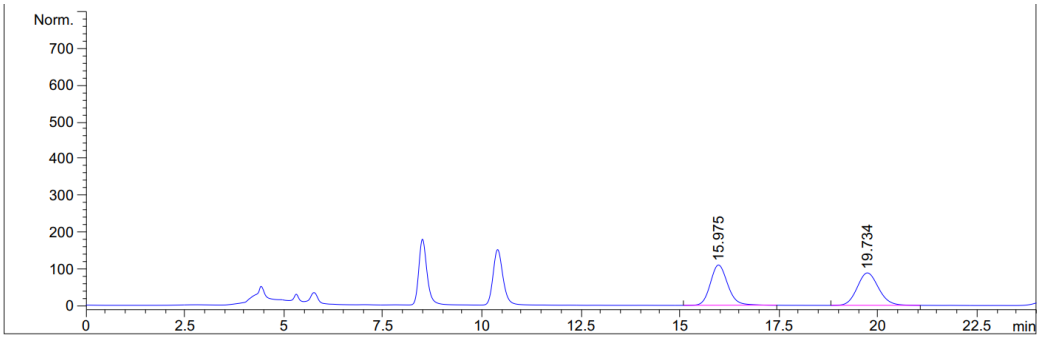


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.346	VV	0.4460	1.19897e4	408.24005	22.3559
2	10.685	VB	0.4839	4.16416e4	1296.66760	77.6441

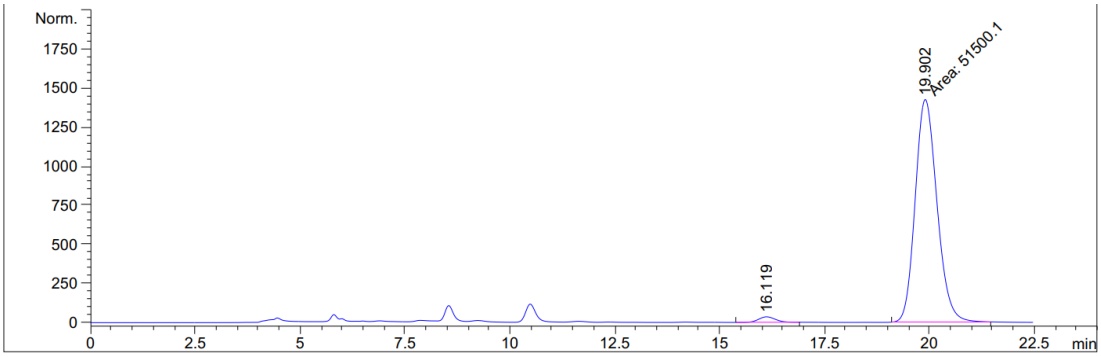
KR-Compound 12c

Prepared according to the procedure within 168 h as white solid (27.8 mg, 34% yield, dr > 20:1); mp 129.9-130.8 °C; $[\alpha]_D^{18}$= -28.80 (*c* 0.28, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.47-8.41 (m, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.65-7.51 (m, 7H), 7.40 (s, 1H), 7.34-7.26 (m, 4H), 7.21-7.17 (m, 2H), 7.16-7.11 (m, 3H), 7.09-7.02 (m, 5H), 7.00-

6.96 (m, 2H), 6.72-6.66 (m, 2H), 5.36 (d, *J* = 9.5 Hz, 1H), 5.20 (d, *J* = 7.7 Hz, 1H), 5.11 (d, *J* = 11.8 Hz, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.62-4.55 (m, 1H), 3.74 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 173.4, 159.8, 155.1, 151.3, 138.2, 137.4, 136.2, 136.0, 135.6, 134.1, 133.8, 131.8, 130.9, 130.5, 130.3, 130.1, 129.3, 128.8, 128.7, 128.7, 128.5, 128.3, 128.1, 128.0, 127.3, 126.9, 126.5, 125.3, 125.2, 123.5, 123.2, 118.9, 118.8, 113.9, 71.7, 68.0, 63.1, 56.4, 55.2, 48.3, 21.0; HRMS (ESI) *m/z* Calcd. for $C_{53}H_{44}N_3O_6^+$ ($[M+H]^+$) 818.3225, Found 818.3219; Enantiomeric excess was determined to be 97% (determined by HPLC using chiral IA column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 19.9 min, t_{minor} = 16.1 min).

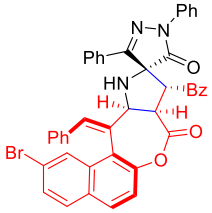


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.975	BB	0.4725	3363.46851	109.77303	50.3180
2	19.734	BB	0.5885	3320.94946	88.34985	49.6820



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.119	PB	0.4364	980.31342	35.26645	1.8680
2	19.902	MM	0.6032	5.15001e4	1422.96973	98.1320

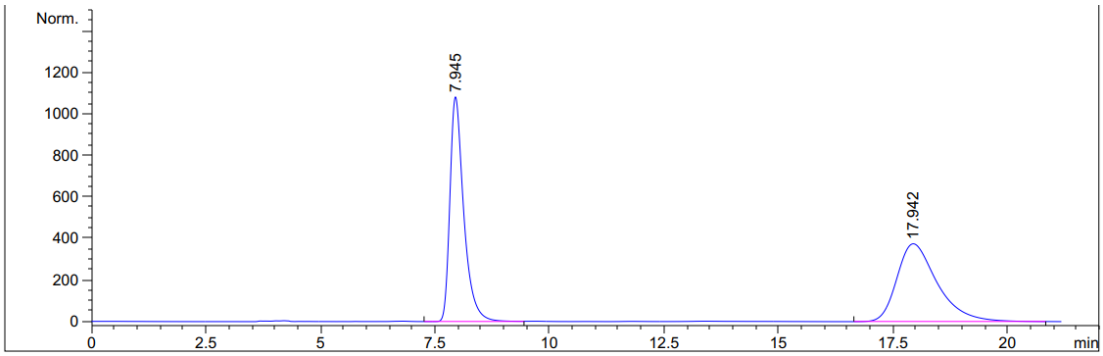
KR-Compound (–)-3ia



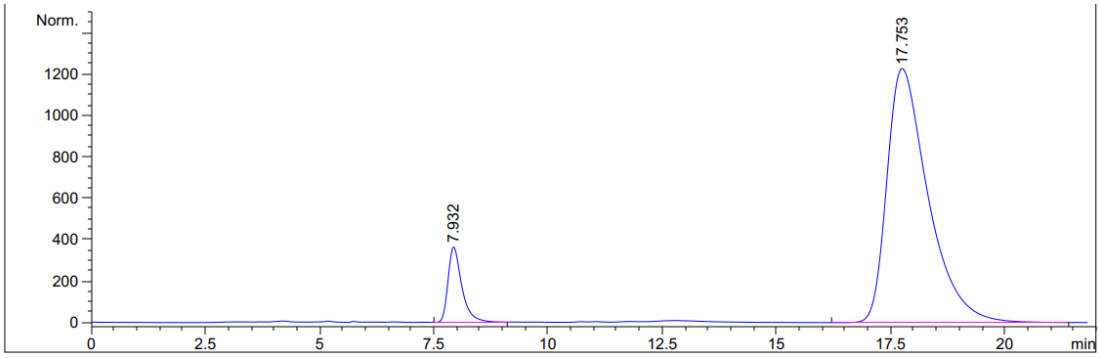
(-)-3ia

Prepared according to the procedure within 168 h as white solid (34.3 mg, 46% yield); $[\alpha]_D^{18}$ = -10.04 (*c* 0.44, CH_2Cl_2); Enantiomeric excess was determined to be 81% (determined by

HPLC using chiral AD-H column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 17.8 min, t_{minor} = 7.9 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.945	VB	0.3156	2.28032e4	1082.72888	49.8342
2	17.942	BB	0.9193	2.29550e4	375.06909	50.1658

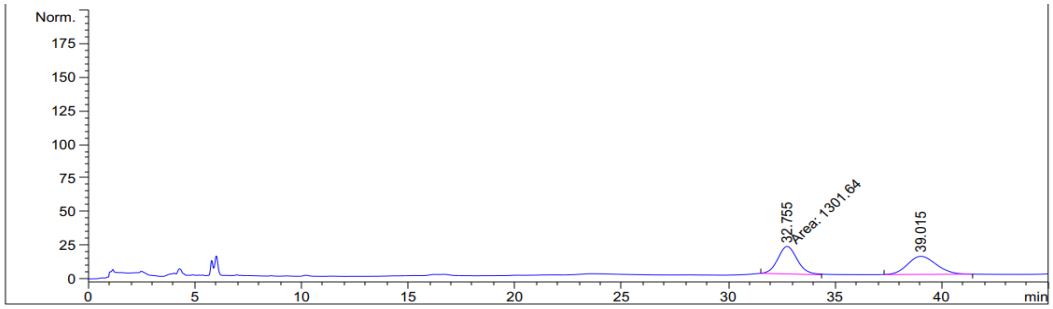


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.932	VV	0.3188	7716.84326	363.82080	9.1300
2	17.753	VB	0.9280	7.68052e4	1227.46497	90.8700

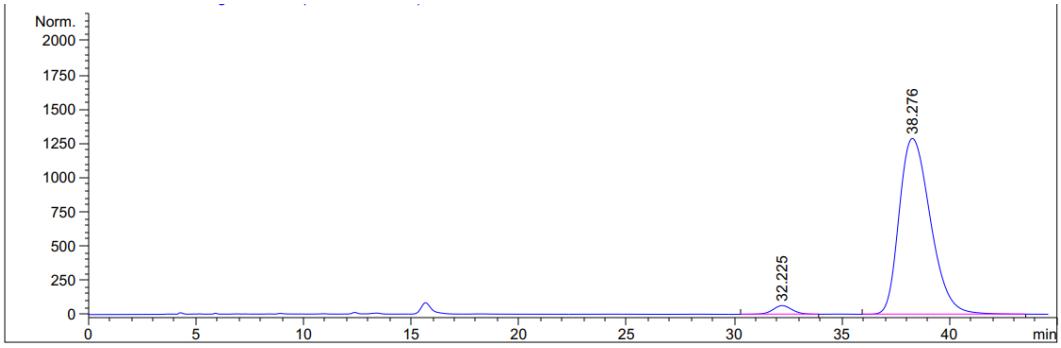
KR-Compound 12d

Prepared according to the procedure within 168 h as white solid (34.4 mg, 39% yield, dr > 20:1); mp 133.9-134.8 °C; $[\alpha]_D^{18}$= -47.60 (*c* 0.46, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43-8.38 (m, 2H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.64-7.62 (m, 2H), 7.61-7.57 (m, 1H), 7.56-7.48 (m, 3H), 7.41-7.29 (m, 7H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.16-7.06 (m, 6H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.71-6.65 (m, 2H), 5.35 (d, *J* = 9.4 Hz, 1H), 5.19 (d, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 11.8 Hz, 1H), 4.89 (d, *J* = 11.8 Hz, 1H), 4.54 (dd, *J* = 9.4, 7.5 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.6, 173.5, 173.4, 159.9, 155.1, 151.8, 137.3, 136.5, 136.4, 135.3, 133.5, 133.1, 131.0, 130.6, 130.4, 130.4, 130.3, 130.2, 130.1, 129.2,

128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.3, 126.4, 125.5, 125.5, 120.1, 119.0, 117.0, 114.0, 71.6, 68.1, 63.1, 56.3, 55.2, 48.4; HRMS (ESI) *m/z* Calcd. for $C_{52}H_{41}BrN_3O_6^+$ ([M+H]$^+$) 882.2173, Found 882.2178; Enantiomeric excess was determined to be 94% (determined by HPLC using chiral IF column, hexane/2-propanol = 70/30, λ = 254 nm, 30 °C, 0.8 mL/min, t_{major} = 38.3 min, t_{minor} = 32.2 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.755	MM	1.0575	1301.64429	20.51410	50.7685
2	39.015	BB	1.1060	1262.23718	13.43867	49.2315



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.225	BB	0.9348	3938.87451	63.11533	2.9448
2	38.276	VB	1.5813	1.29818e5	1284.16846	97.0552

6. References

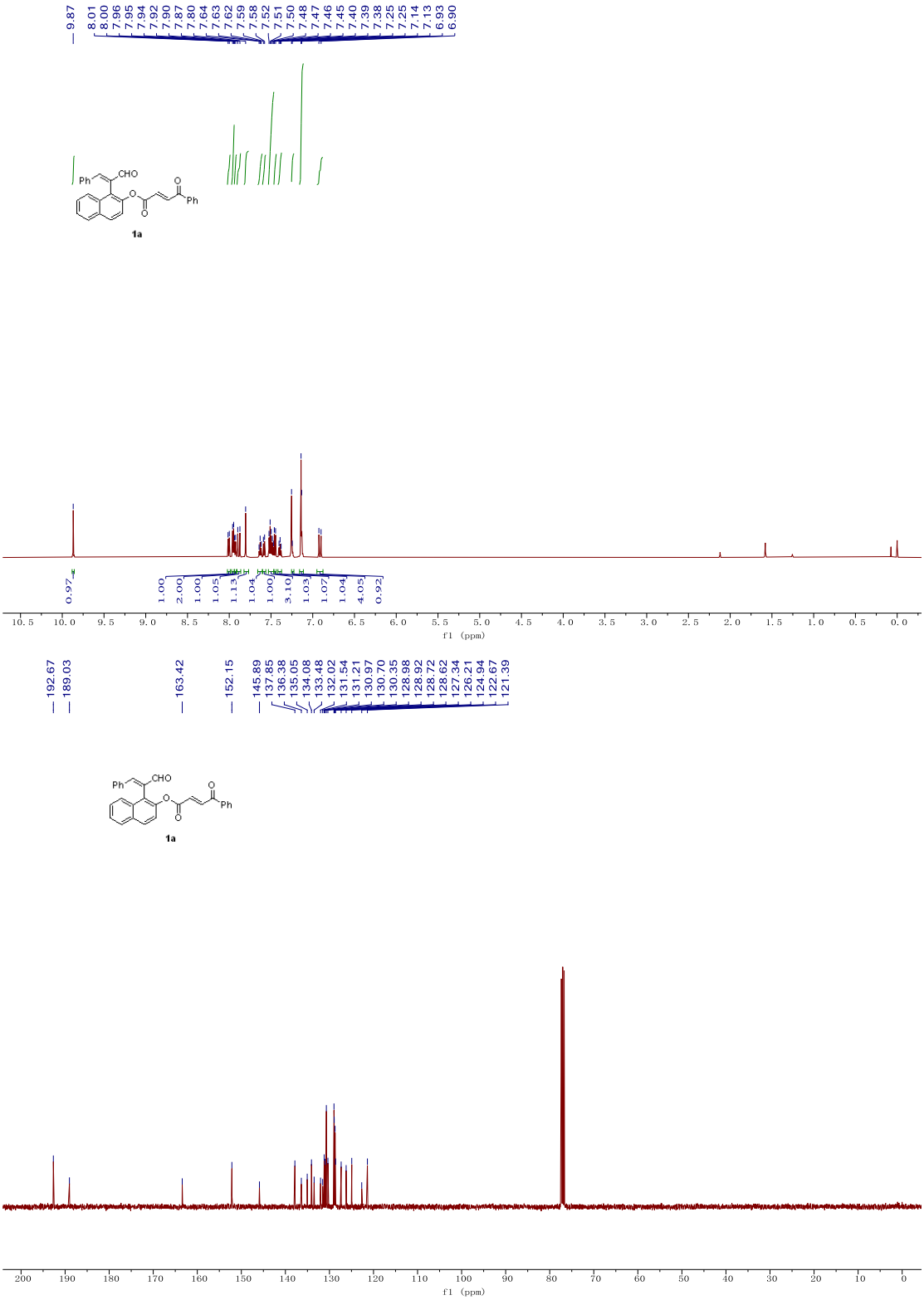
[1] The synthesis of 3-amino oxindole hydrochlorides, see: W. Chen, Z. Wu, J. Hu, L. Cun, X. Zhang, W. Yuan. *Org. Lett*. **2011**, *13*, 2472.

[2] The synthesis of 4-Amino pyrazolone hydrochlorides, see: X. Bao, S. Wei, X. Qian, J. Qu, B. Wang, L. Zou and G. Ge. *Org. Lett.* **2018**, *20*, 3394-3398.

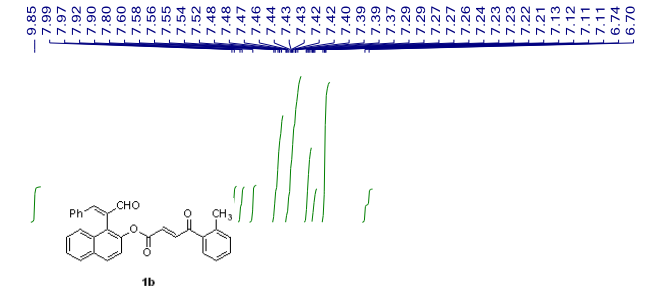
[3] You-Dong Shao，Jin-Shuo Feng, Dan-Dan Han, Kang-Hui Pan, Ling Zhang, Yi-Fan Wang, Zhong-Hui Ma, Pei-Ru Wang, Mingjing Yin and Dao-Juan Cheng. *Org. Chem. Front*. **2022**, *9*, 764-770.

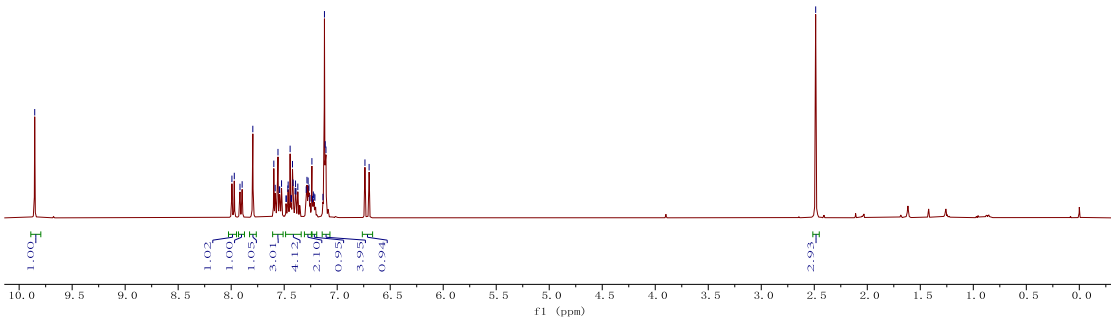
7. NMR spectra for compounds

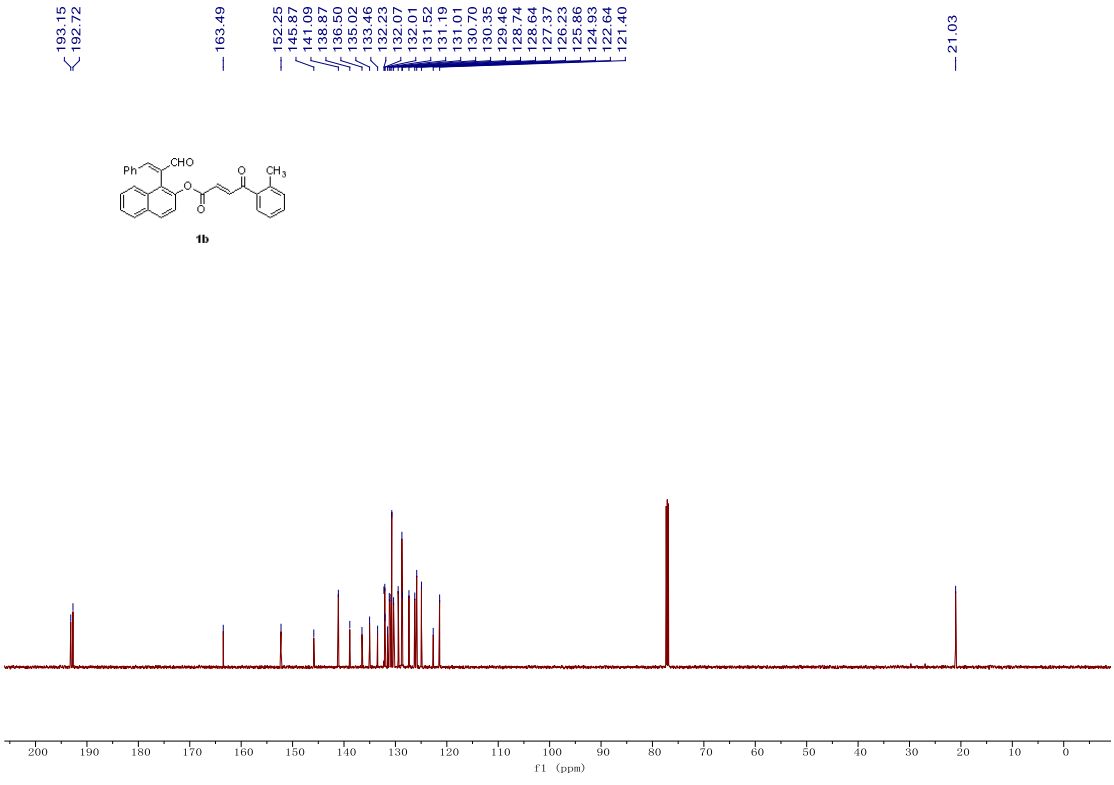
1a



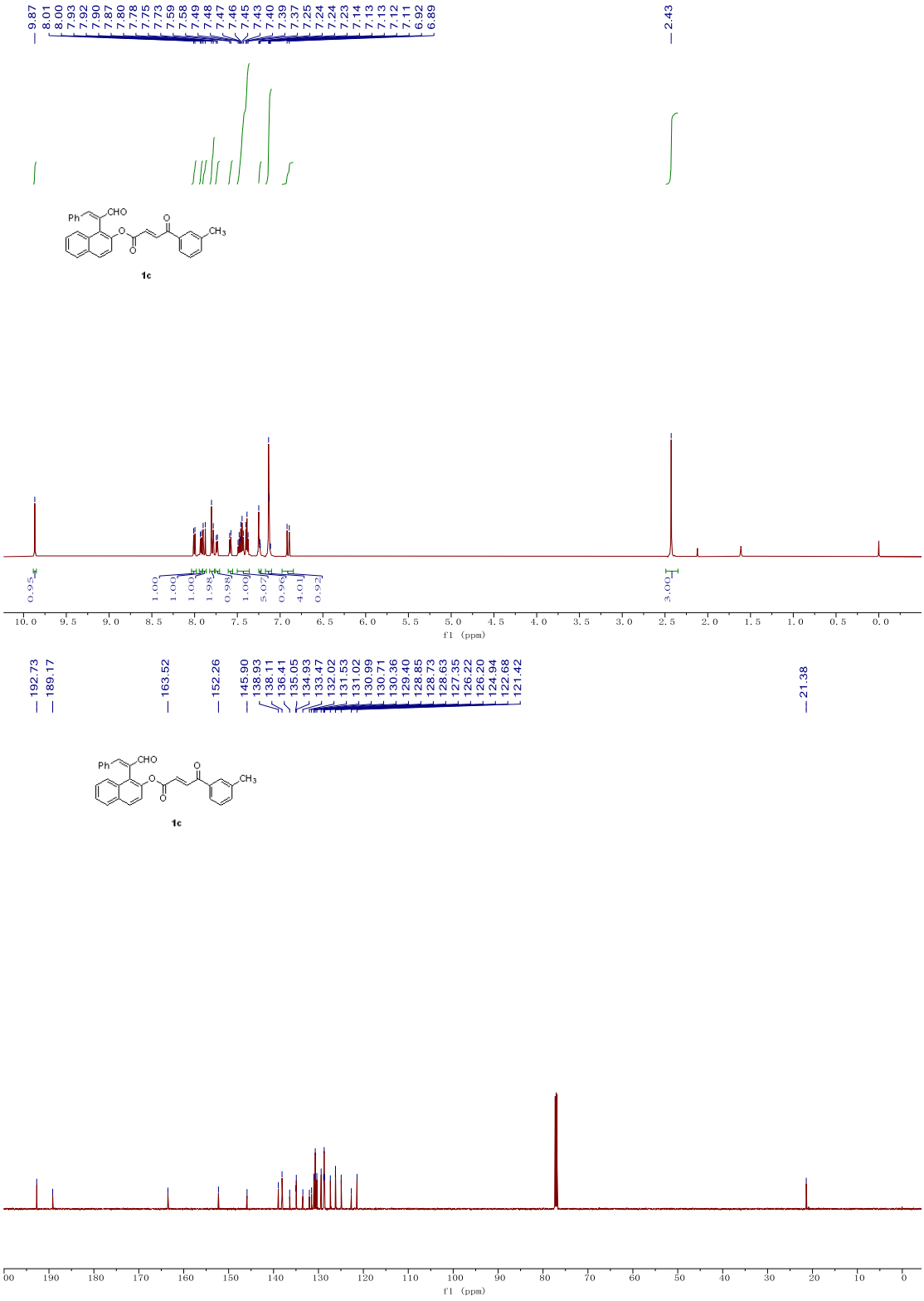
1b


9.85
7.99
7.97
7.92
7.90
7.80
7.60
7.58
7.56
7.55
7.54
7.52
7.48
7.48
7.47
7.46
7.44
7.43
7.43
7.42
7.42
7.40
7.39
7.39
7.37
7.29
7.29
7.27
7.27
7.26
7.24
7.23
7.23
7.22
7.21
7.13
7.12
7.11
7.11
6.74
6.70
2.49
Ph
CHO
O
O
O
CH3
1b


1.00
1.02
1.00
1.05
3.01
4.12
2.10
0.95
3.95
0.94
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

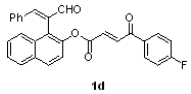

193.15
192.72
163.49
152.25
145.87
141.09
138.87
136.50
135.02
133.46
132.23
132.07
132.01
131.52
131.19
131.01
130.70
130.35
129.46
128.74
128.64
127.37
126.23
125.86
124.93
122.64
121.40
21.03
Ph
CHO
O
O
O
CH3
1b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1c

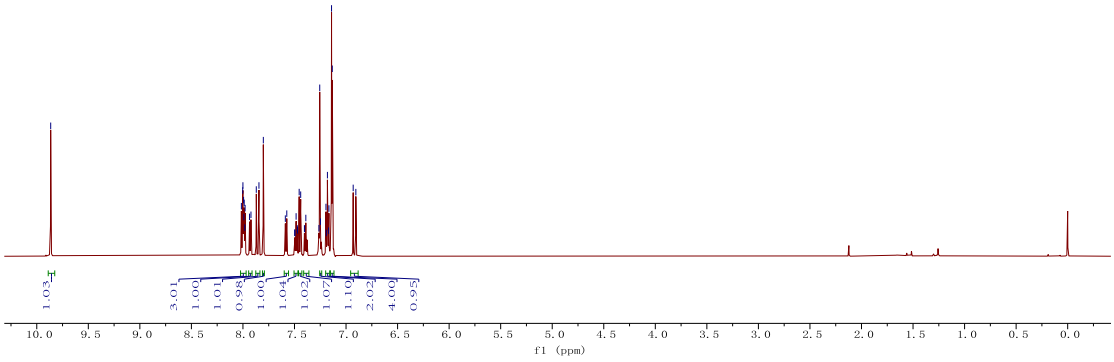

9.87
8.01
8.00
7.93
7.92
7.90
7.87
7.80
7.78
7.75
7.73
7.59
7.58
7.49
7.48
7.47
7.46
7.45
7.43
7.40
7.39
7.37
7.25
7.24
7.24
7.23
7.14
7.13
7.13
7.12
7.11
6.92
6.89
2.43
Ph
CHO
O
O
O
CH3
1c
0.95
1.00
1.00
1.00
1.98
0.98
1.00
5.07
0.96
4.01
0.92
3.00
f1 (ppm)
192.73
189.17
163.52
152.26
145.90
138.93
138.11
136.41
135.05
134.93
133.47
132.02
131.53
131.02
130.99
130.71
130.36
129.40
128.85
128.73
128.63
127.35
126.22
126.20
124.94
122.68
121.42
21.38
Ph
CHO
O
O
O
CH3
1c
f1 (ppm)

1d

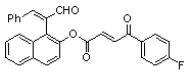

9.86
8.02
8.00
8.00
7.99
7.99
7.98
7.98
7.94
7.92
7.87
7.84
7.80
7.59
7.57
7.50
7.50
7.48
7.47
7.47
7.45
7.44
7.40
7.40
7.39
7.26
7.25
7.19
7.18
7.17
7.17
7.14
7.13
6.93
6.90


Ph
CHO
O
O
O
F

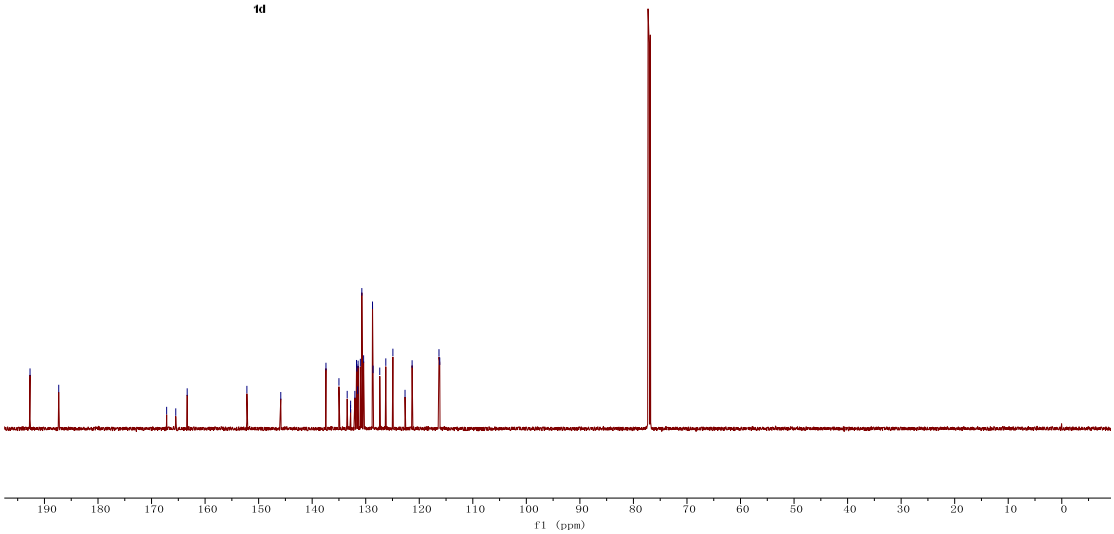
1d


1.03
3.01
1.00
1.01
0.98
1.00
1.04
1.02
1.07
1.10
2.02
4.00
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

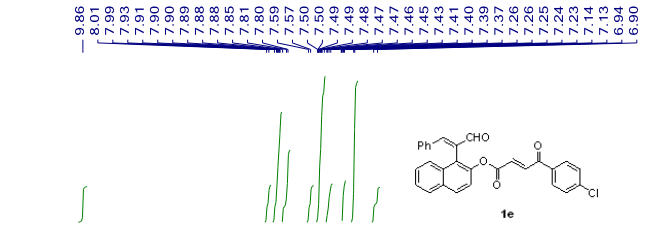

192.70
187.34
167.18
165.48
163.34
152.19
145.87
137.43
135.00
133.46
132.84
132.82
132.03
131.72
131.65
131.50
131.42
131.00
130.72
130.39
128.73
128.63
127.38
126.25
124.93
122.66
121.33
116.32
116.17

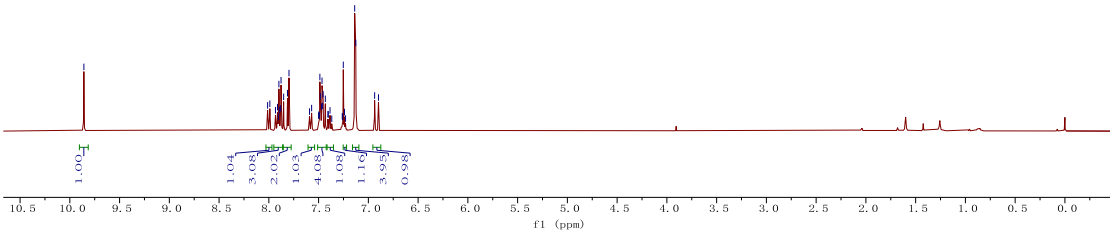

Ph
CHO
O
O
O
F

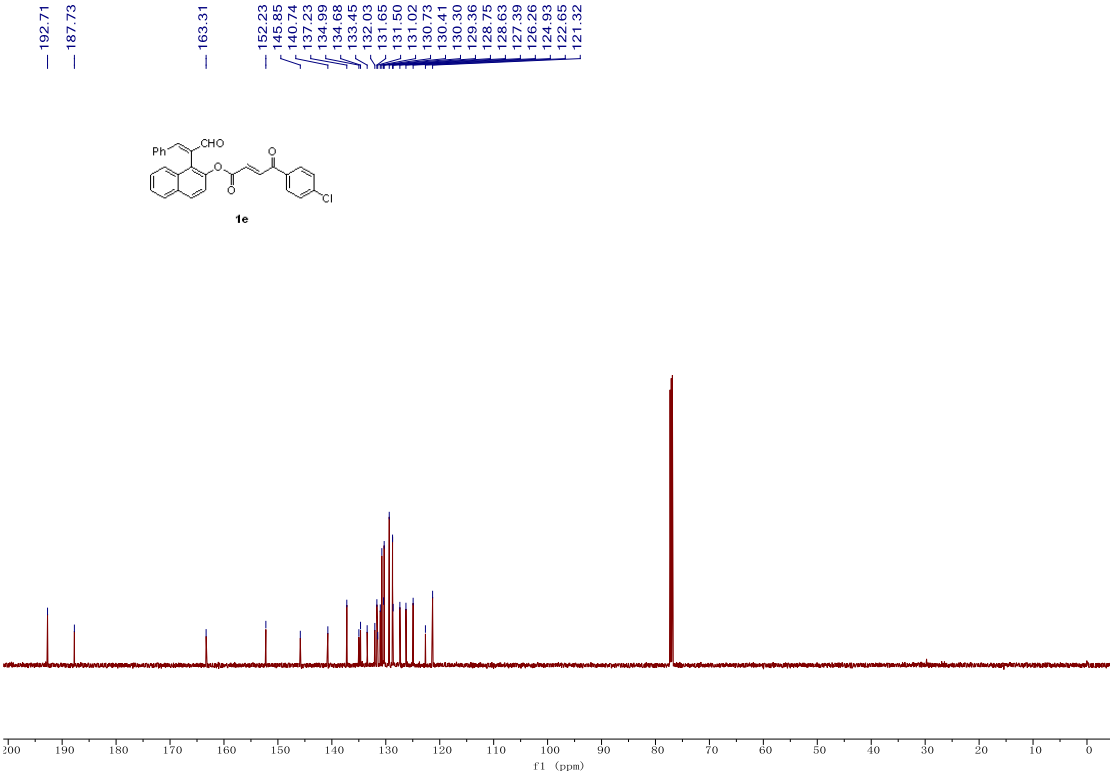
1d


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

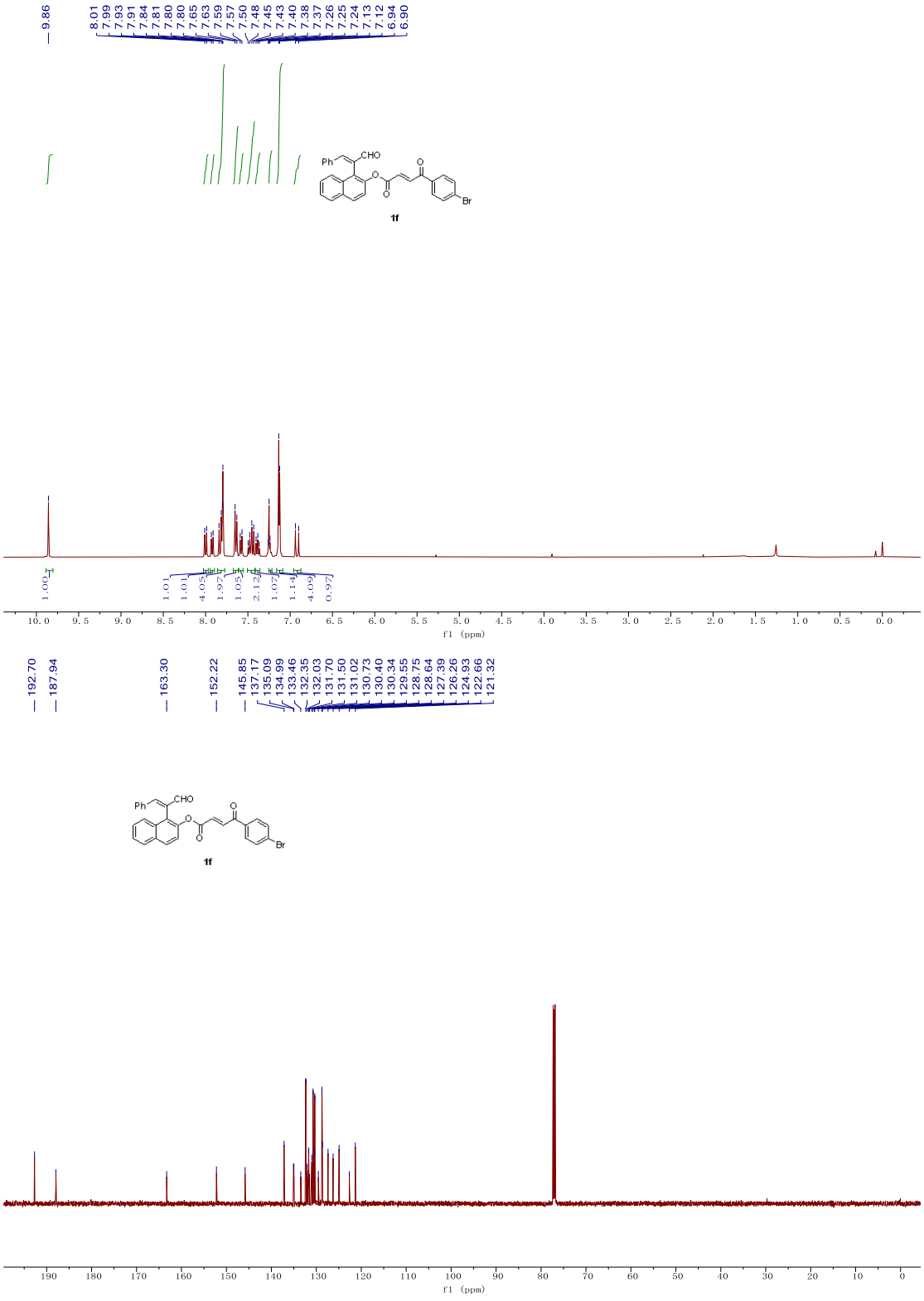
1e


9.86
8.01
7.99
7.93
7.91
7.90
7.90
7.89
7.88
7.88
7.85
7.81
7.80
7.59
7.57
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.43
7.41
7.40
7.39
7.37
7.26
7.26
7.25
7.24
7.23
7.14
7.13
6.94
6.90
Ph
CHO
O
O
O
Cl
1e

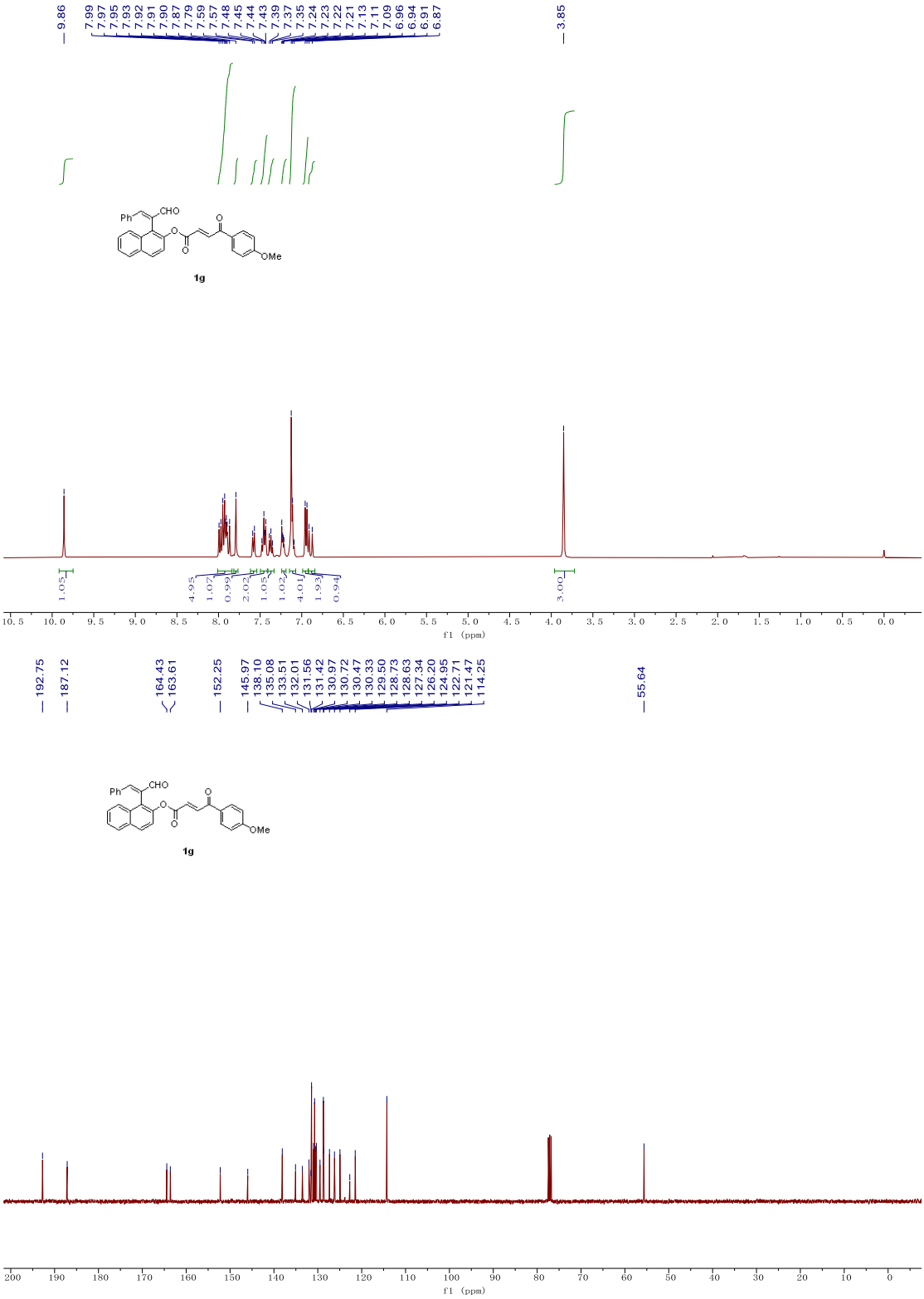

1.00
1.04
3.08
2.02
1.03
4.08
1.08
1.16
3.95
0.98
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.71
187.73
163.31
152.23
145.85
140.74
137.23
134.99
134.88
133.45
132.03
131.65
131.50
131.02
130.73
130.41
130.30
129.36
128.75
128.63
127.39
126.26
124.93
122.65
121.32
Ph
CHO
O
O
O
Cl
1e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

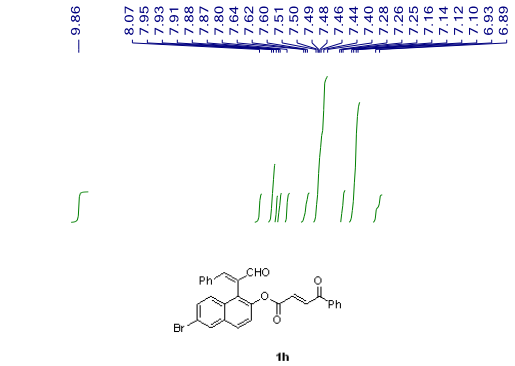
1f

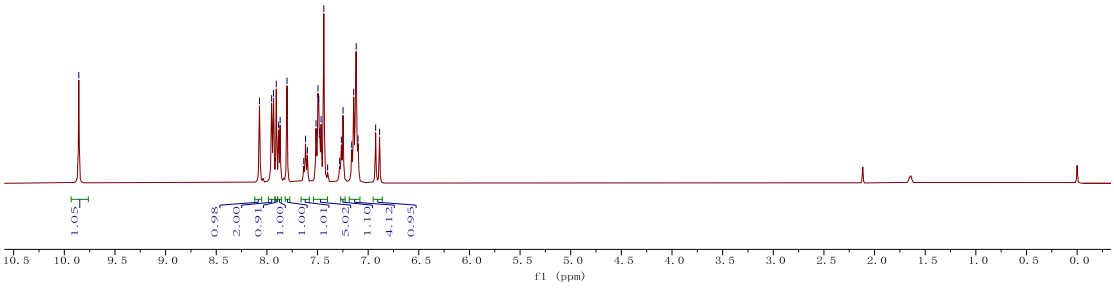

9.86
8.01
7.99
7.93
7.91
7.84
7.81
7.80
7.80
7.65
7.63
7.59
7.57
7.50
7.48
7.45
7.43
7.40
7.38
7.37
7.26
7.25
7.24
7.13
7.12
6.94
6.90
Ph
CHO
O
O
O
Br
1f
1.00
1.01
1.01
4.05
1.97
1.05
2.12
1.07
1.14
4.09
0.97
f1 (ppm)
192.70
187.94
163.30
152.22
145.85
137.17
135.09
134.99
133.46
132.35
132.03
131.70
131.50
131.02
130.73
130.40
130.34
129.55
128.75
128.64
127.39
126.26
124.93
122.66
121.32
Ph
CHO
O
O
O
Br
1f
f1 (ppm)

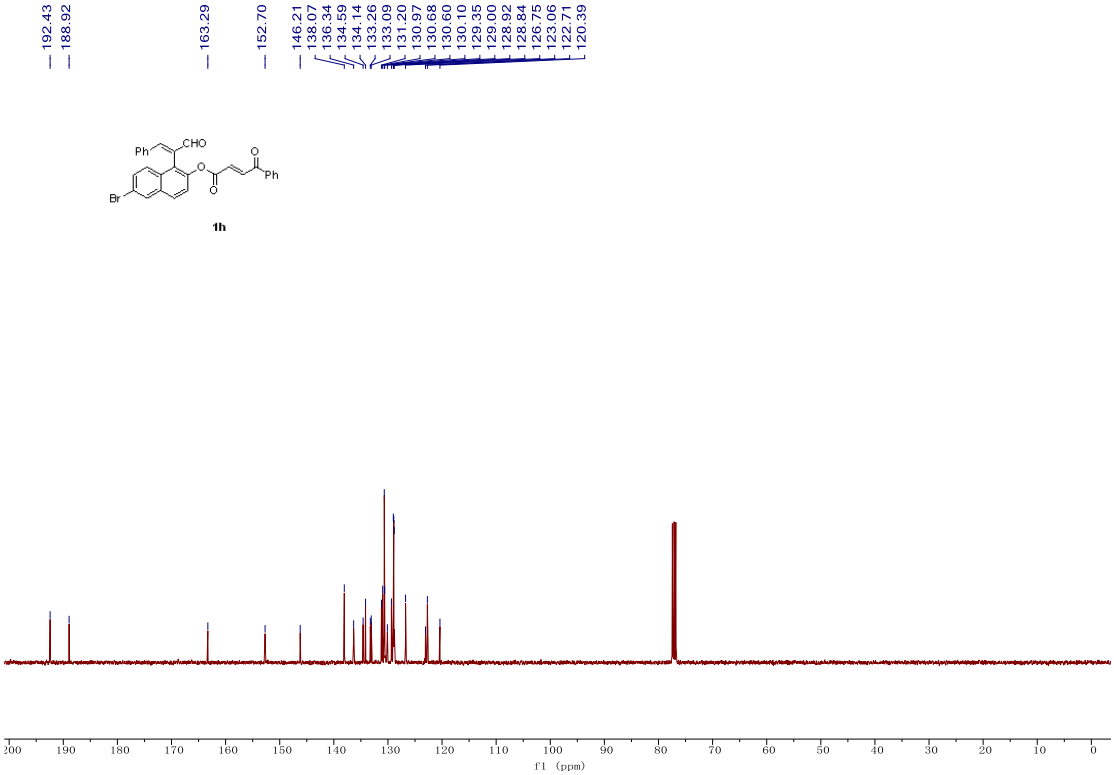
1g


9.86
7.99
7.97
7.95
7.93
7.92
7.91
7.90
7.87
7.79
7.59
7.57
7.48
7.45
7.44
7.43
7.39
7.37
7.35
7.24
7.23
7.22
7.21
7.13
7.11
7.09
6.96
6.94
6.91
6.87
3.85
Ph
CHO
O
O
O
OMe
1g
1.05
4.95
1.07
0.99
2.02
1.05
1.02
4.01
1.93
0.94
3.00
f1 (ppm)
192.75
187.12
164.43
163.61
152.25
145.97
138.10
135.08
133.51
132.01
131.56
131.42
130.97
130.72
130.47
130.33
129.50
128.73
128.63
127.34
126.20
124.95
122.71
121.47
114.25
55.64
Ph
CHO
O
O
O
OMe
1g
f1 (ppm)

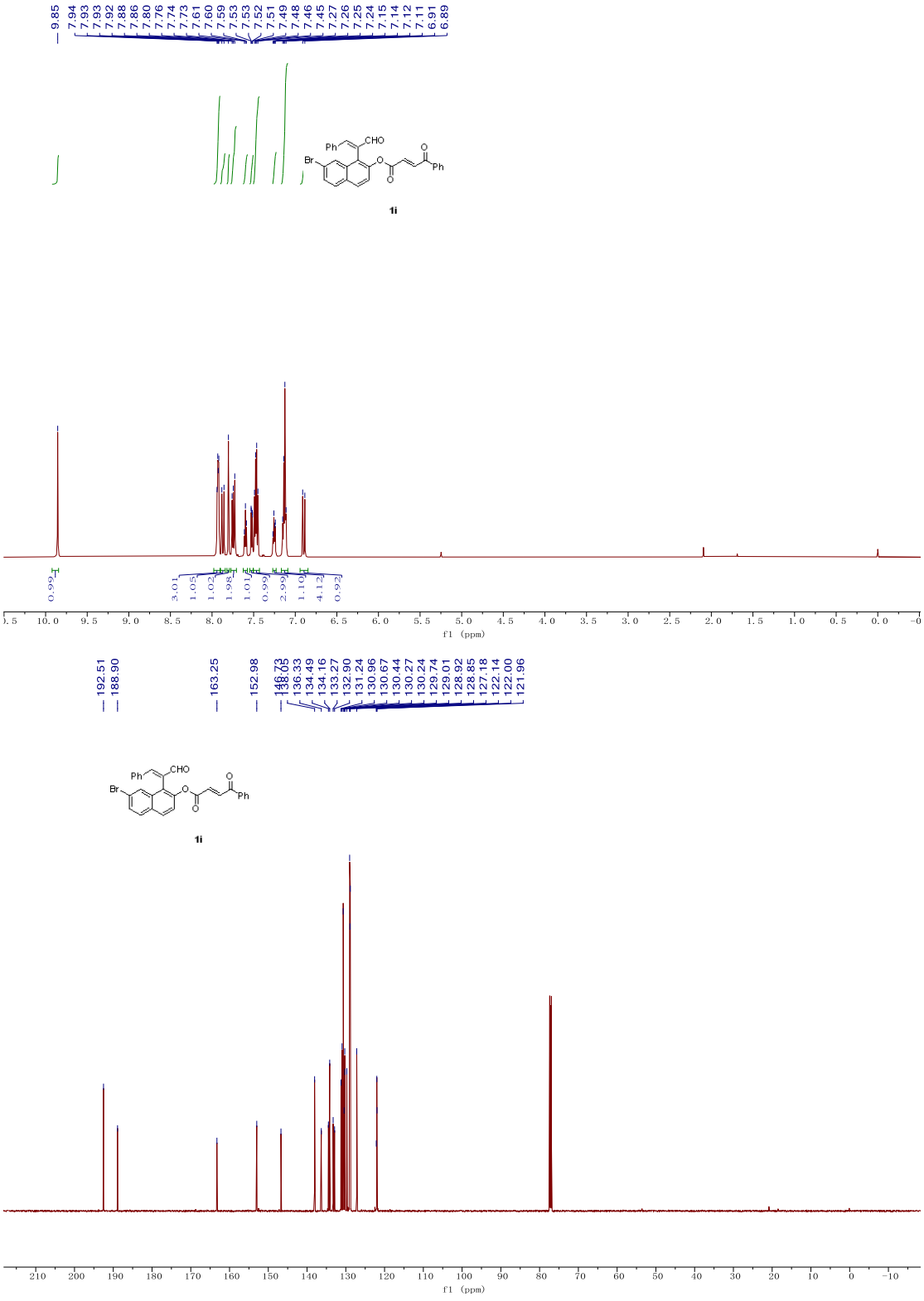
1h


9.86
8.07
7.95
7.93
7.91
7.88
7.87
7.80
7.64
7.62
7.60
7.51
7.50
7.49
7.48
7.46
7.44
7.40
7.28
7.26
7.25
7.16
7.14
7.12
7.10
6.93
6.89
Ph
CHO
O
O
Ph
Br
1h

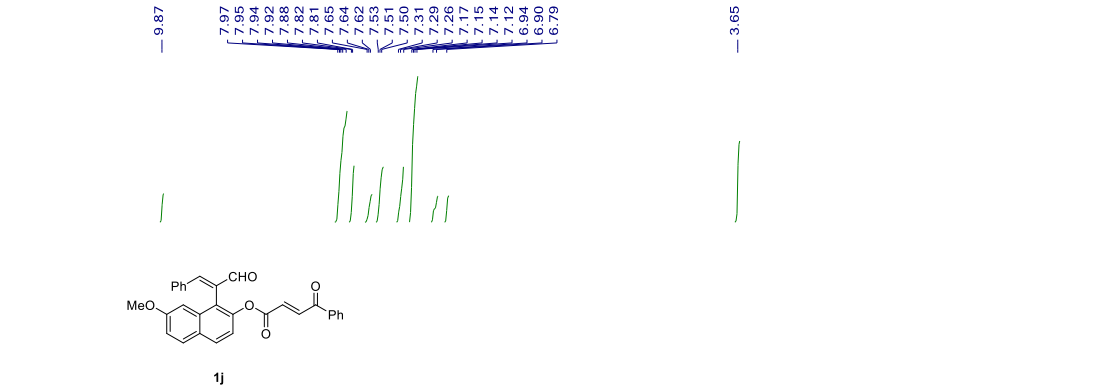

1.05
0.98
2.00
0.91
1.00
1.00
1.01
5.02
1.10
4.12
0.95
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.43
188.92
163.29
152.70
146.21
138.07
136.34
134.59
134.14
133.26
133.09
131.20
130.97
130.68
130.60
130.10
129.35
129.00
128.92
128.84
126.75
123.06
122.71
120.39
Ph
CHO
O
O
Ph
Br
1h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

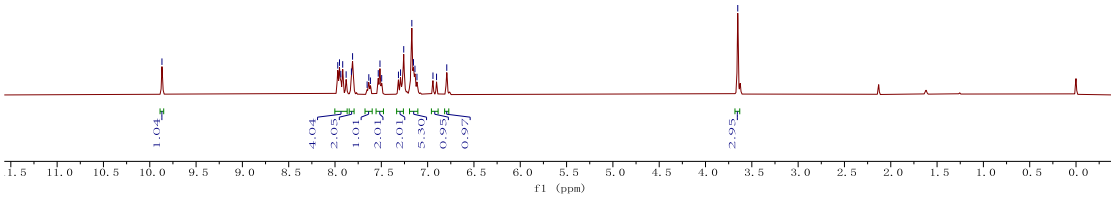
1i


9.85
7.94
7.93
7.93
7.92
7.88
7.86
7.80
7.76
7.74
7.73
7.61
7.60
7.59
7.53
7.53
7.52
7.51
7.49
7.48
7.46
7.45
7.27
7.26
7.25
7.24
7.15
7.14
7.12
7.11
6.91
6.89
Ph
CHO
Br
O
O
O
Ph
1i
0.99
3.01
1.05
1.02
1.98
1.01
0.99
2.99
1.10
4.12
0.92
f1 (ppm)
192.51
188.90
163.25
152.98
146.73
138.05
136.33
134.49
134.16
133.27
132.90
131.24
130.96
130.67
130.44
130.27
130.24
129.74
129.01
128.92
128.85
127.18
122.14
122.00
121.96
Ph
CHO
Br
O
O
O
Ph
1i
f1 (ppm)

1j


9.87
7.97
7.95
7.94
7.92
7.88
7.82
7.81
7.65
7.64
7.62
7.53
7.51
7.50
7.31
7.29
7.26
7.17
7.15
7.14
7.12
6.94
6.90
6.79
3.65
Ph
CHO
MeO
O
O
O
Ph

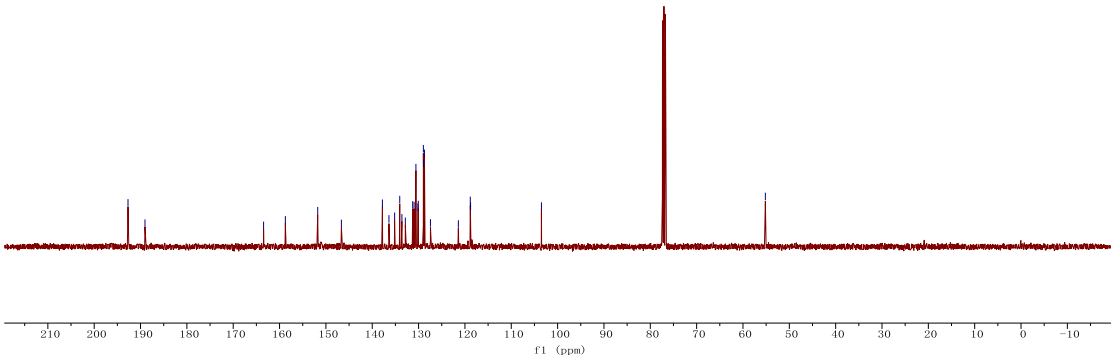
1j


1.04
4.04
2.05
1.01
2.01
2.01
5.30
0.95
0.97
2.95
f1 (ppm)

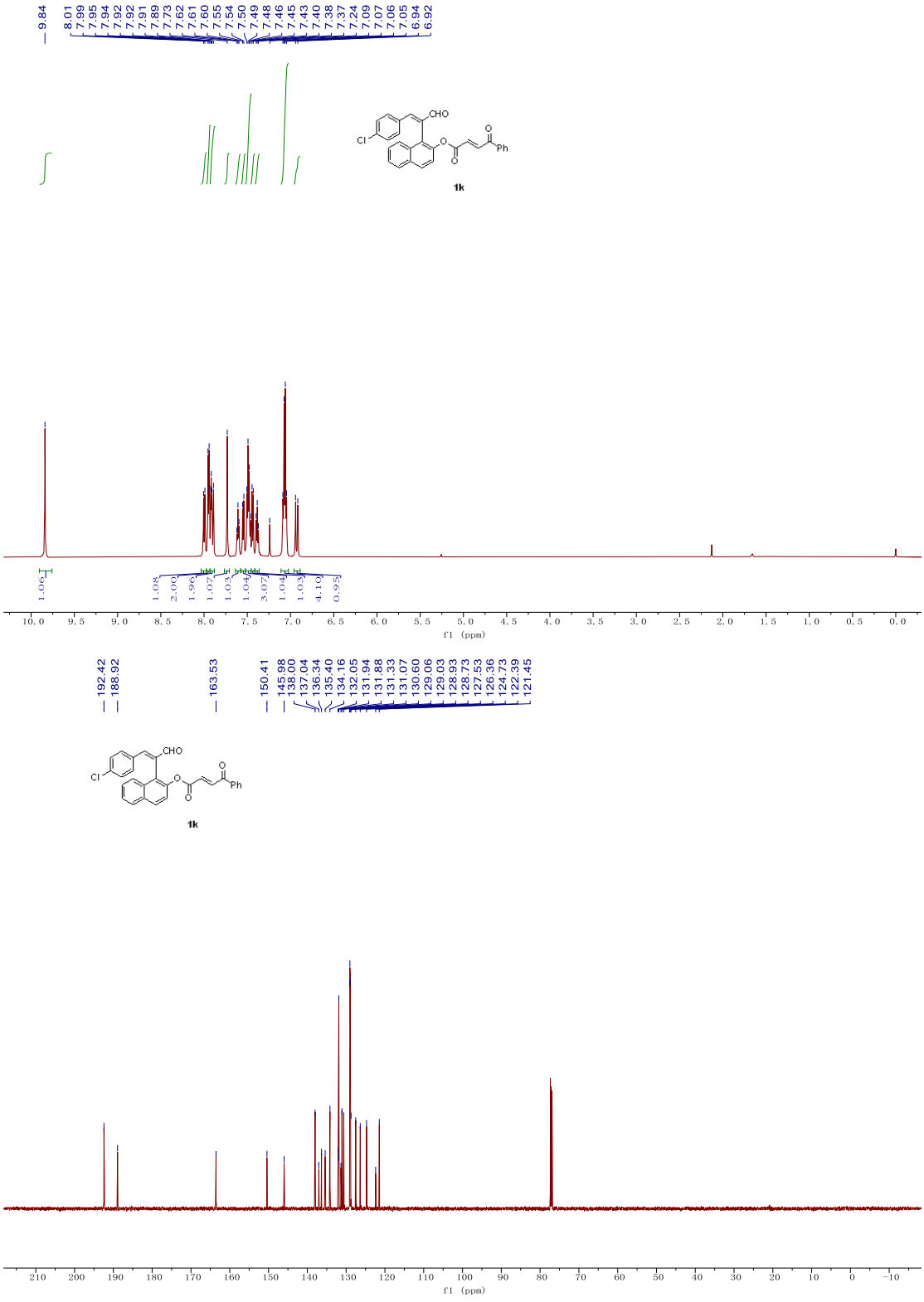

192.70
189.04
163.45
158.75
151.77
146.66
137.80
136.40
135.17
134.06
133.60
132.86
131.27
130.97
130.57
130.15
130.06
128.97
128.92
128.74
127.44
121.42
118.84
118.78
103.49
55.17


Ph
CHO
MeO
O
O
O
Ph

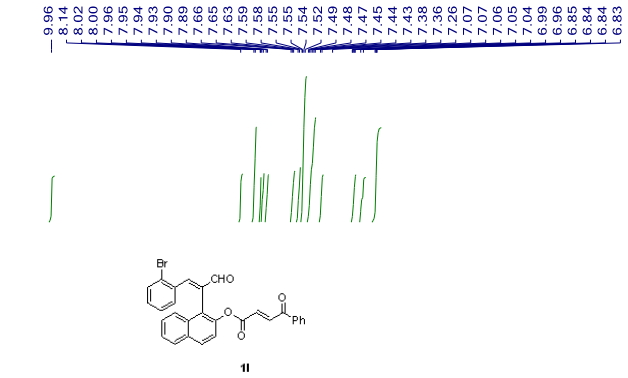
1j


f1 (ppm)

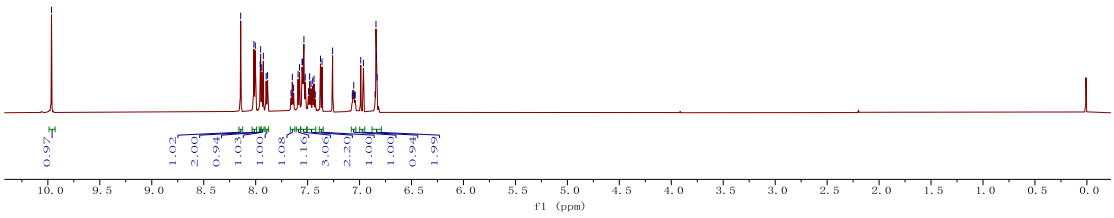
1k

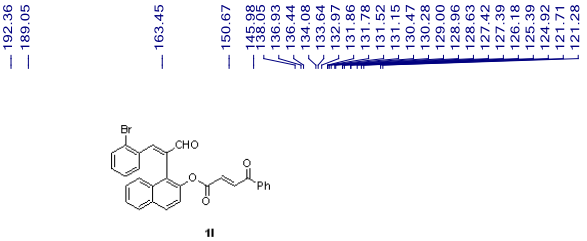

9.84
8.01
7.99
7.95
7.94
7.92
7.91
7.89
7.73
7.62
7.61
7.60
7.55
7.54
7.50
7.49
7.48
7.46
7.45
7.43
7.40
7.38
7.37
7.24
7.09
7.07
7.06
7.05
6.94
6.92
CHO
Cl
O
O
O
Ph
1k
1.06
1.08
2.00
1.96
1.07
1.03
1.04
3.07
1.04
1.03
4.10
0.95
f1 (ppm)
192.42
188.92
163.53
150.41
145.98
138.00
137.04
136.34
135.40
134.16
132.05
131.94
131.88
131.33
131.07
130.60
129.06
129.03
128.93
128.73
127.53
126.36
124.73
122.39
121.45
CHO
Cl
O
O
O
Ph
1k
f1 (ppm)

1l

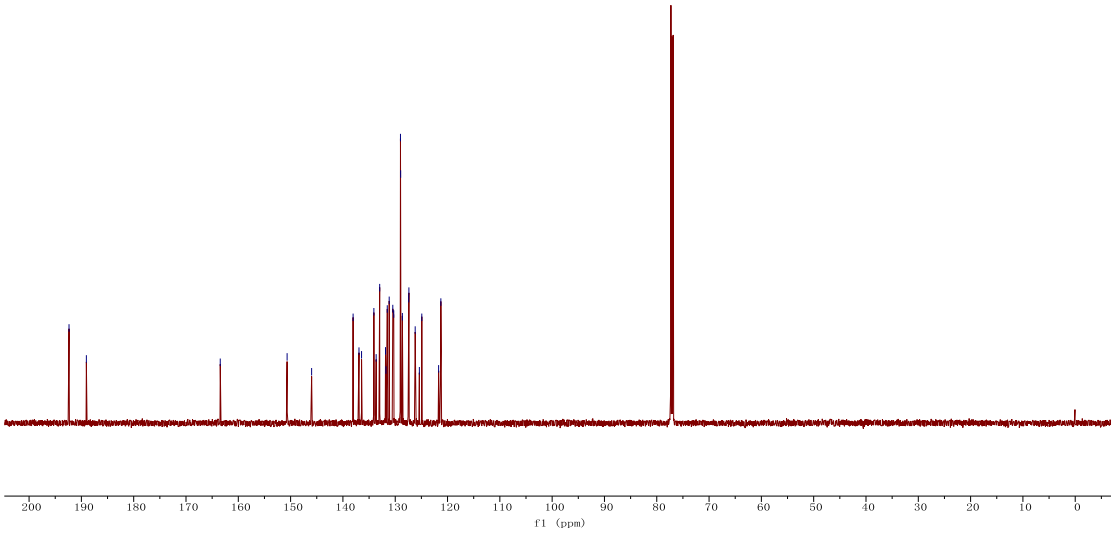

9.96
8.14
8.02
8.00
7.96
7.95
7.94
7.93
7.90
7.89
7.66
7.65
7.63
7.59
7.58
7.55
7.55
7.54
7.52
7.49
7.48
7.47
7.45
7.44
7.43
7.38
7.36
7.26
7.07
7.07
7.06
7.05
7.04
6.99
6.96
6.85
6.84
6.84
6.83
Br
CHO
O
O
O
Ph

1l

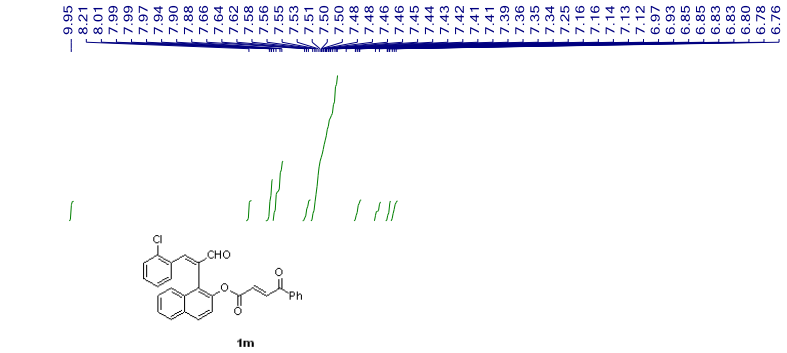

0.97
1.03
2.00
0.94
1.03
1.00
1.08
1.16
3.06
2.20
1.00
1.00
0.94
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

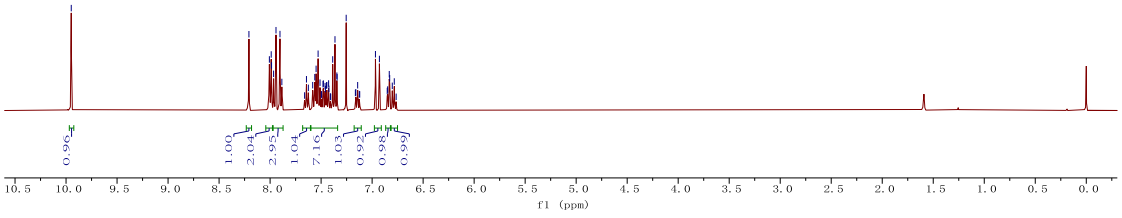

192.36
189.05
163.45
150.67
145.98
138.05
136.93
136.44
134.08
133.64
132.97
131.86
131.78
131.52
131.15
130.47
130.28
129.00
128.96
128.63
127.42
127.39
126.18
125.39
124.92
121.71
121.28
Br
CHO
O
O
O
Ph

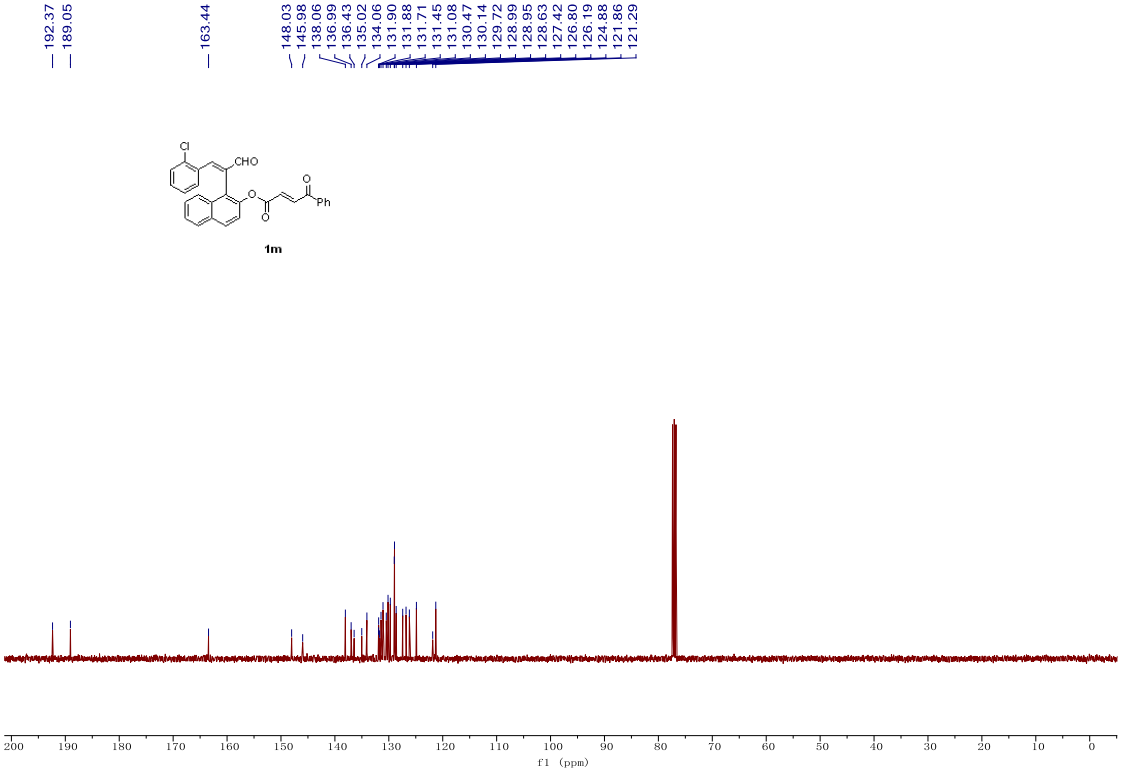
1l


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

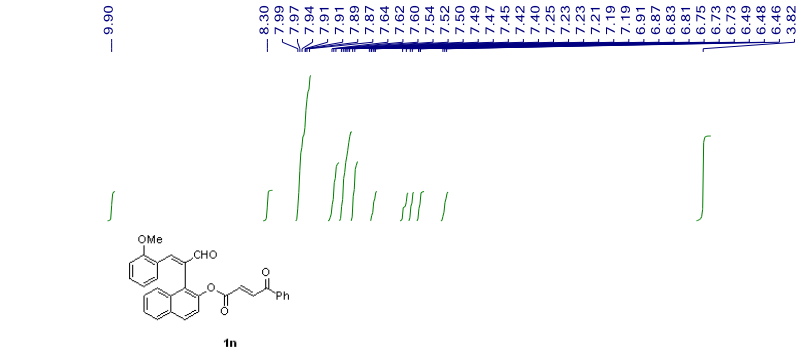
1m

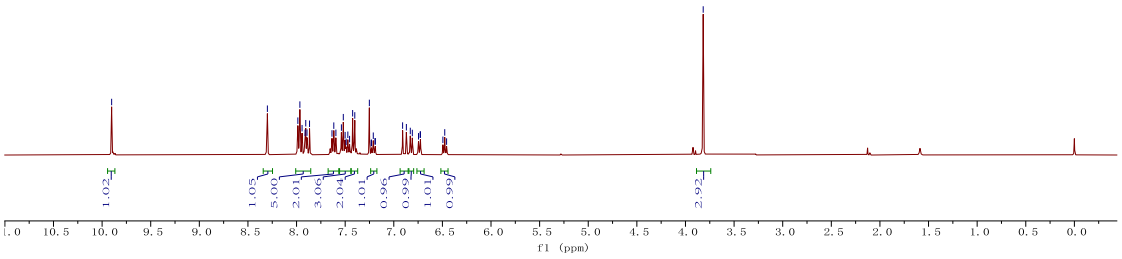

9.95
8.21
8.01
7.99
7.99
7.97
7.94
7.90
7.88
7.66
7.64
7.62
7.58
7.56
7.55
7.53
7.51
7.50
7.50
7.48
7.48
7.46
7.46
7.45
7.44
7.43
7.42
7.41
7.41
7.39
7.36
7.35
7.34
7.25
7.16
7.16
7.14
7.13
7.12
6.97
6.93
6.85
6.85
6.83
6.83
6.80
6.78
6.76
Cl
CHO
O
O
O
Ph
1m

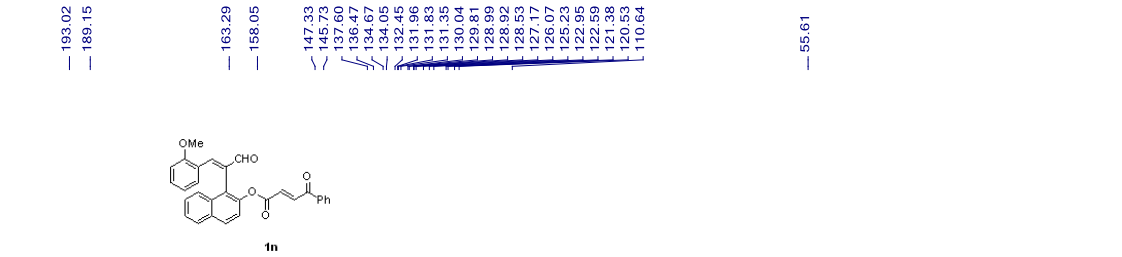

0.96
1.00
2.04
2.95
1.04
7.16
1.03
0.92
0.98
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

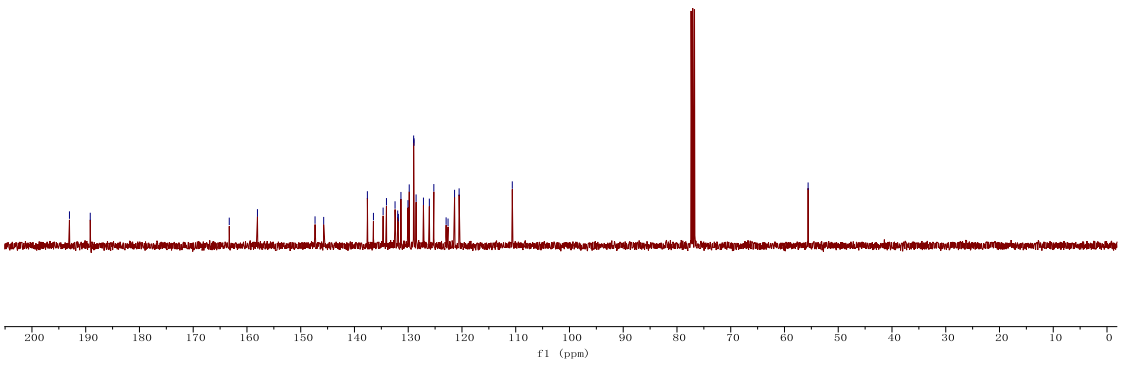

192.37
189.05
163.44
148.03
145.98
138.06
136.99
136.43
135.02
134.06
131.90
131.88
131.71
131.45
131.08
130.47
130.14
129.72
128.99
128.95
128.63
127.42
126.80
126.19
124.88
121.86
121.29
Cl
CHO
O
O
O
Ph
1m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1n

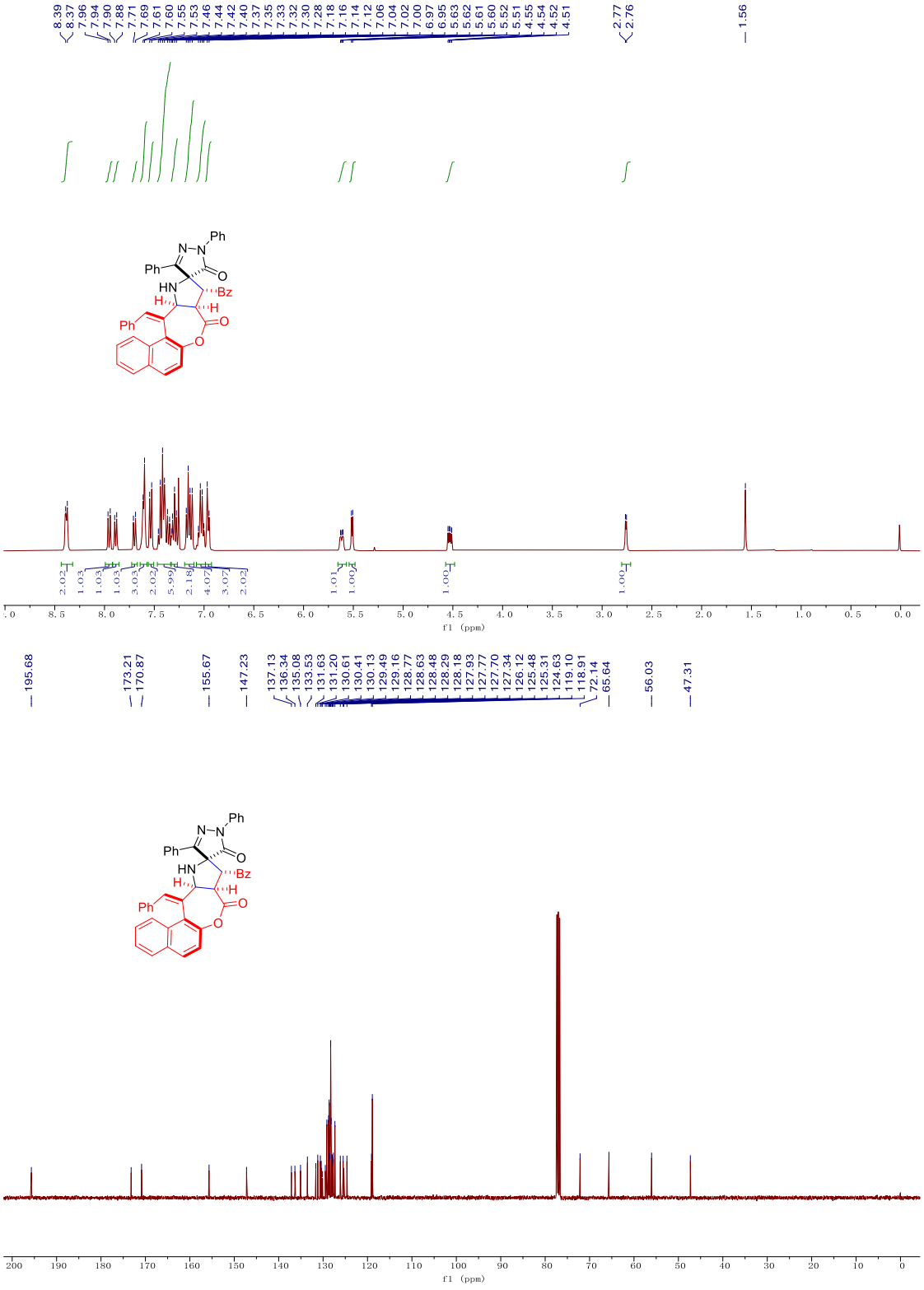

9.90
8.30
7.99
7.97
7.94
7.91
7.91
7.89
7.87
7.64
7.62
7.60
7.54
7.52
7.50
7.49
7.47
7.45
7.42
7.40
7.25
7.23
7.23
7.21
7.19
7.19
6.91
6.87
6.83
6.81
6.75
6.73
6.73
6.49
6.48
6.46
3.82
OMe
CHO
O
O
O
Ph
1n


1.02
1.05
5.00
2.01
3.06
2.04
1.01
0.96
0.93
1.01
0.99
2.92
f1 (ppm)

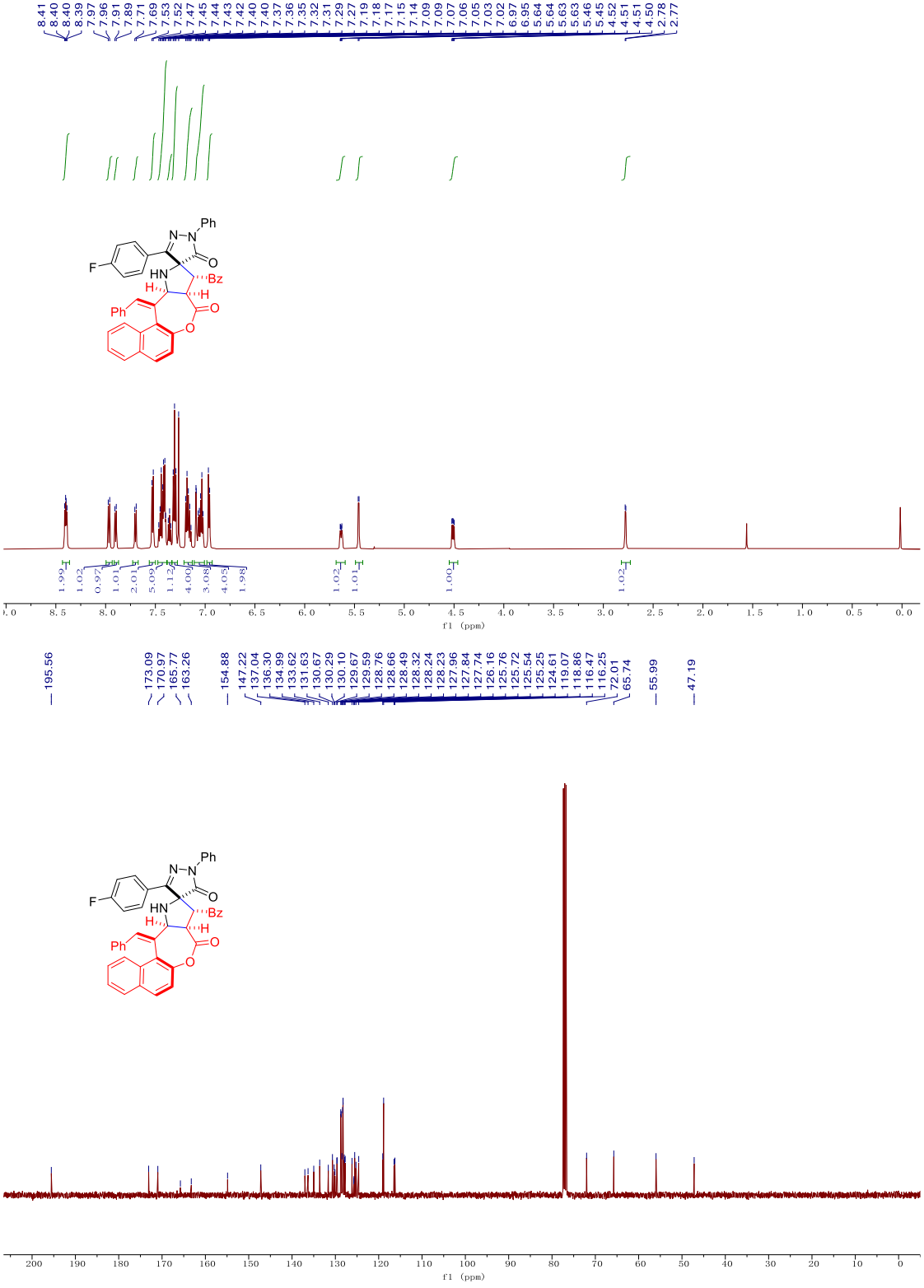

193.02
189.15
163.29
158.05
147.33
145.73
137.60
136.47
134.67
134.05
132.45
131.96
131.83
131.35
130.04
129.81
128.99
128.92
128.53
127.17
126.07
125.23
122.95
122.59
121.38
120.53
110.64
55.61
OMe
CHO
O
O
O
Ph
1n


f1 (ppm)

3aa

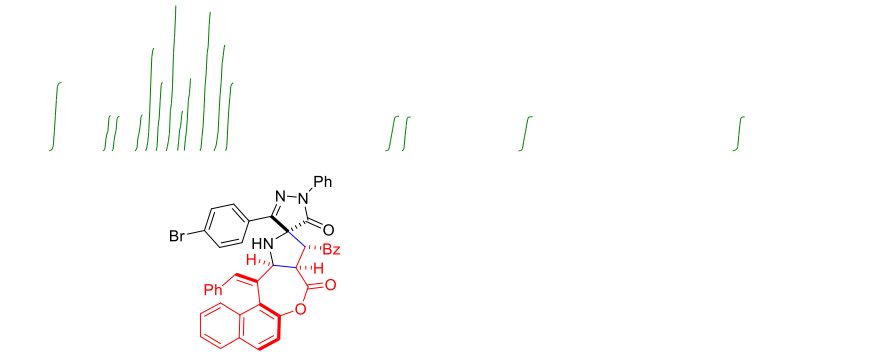

8.39
8.37
7.96
7.94
7.90
7.88
7.71
7.69
7.61
7.60
7.55
7.53
7.46
7.44
7.42
7.40
7.37
7.35
7.33
7.32
7.30
7.28
7.18
7.16
7.14
7.12
7.06
7.04
7.02
7.00
6.97
6.95
5.63
5.62
5.61
5.60
5.52
5.51
4.55
4.54
4.52
4.51
2.77
2.76
1.56
Ph
N
N
Ph
O
HN
H
Bz
H
Ph
O
O
2.02
1.03
1.03
1.03
3.03
2.02
5.99
2.18
4.07
3.07
2.02
1.01
1.00
1.00
1.00
f1 (ppm)
195.68
173.21
170.87
155.67
147.23
137.13
136.34
135.08
133.53
131.63
131.20
130.61
130.41
130.13
129.49
129.16
128.77
128.63
128.48
128.29
128.18
127.93
127.77
127.70
127.34
126.12
125.48
125.31
124.63
119.10
118.91
72.14
65.64
56.03
47.31
f1 (ppm)

3ab

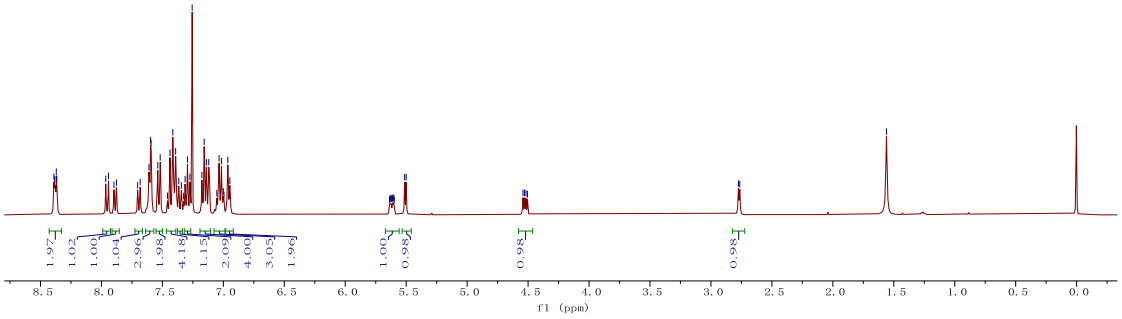

8.41 8.40 8.40 8.39 7.97 7.96 7.91 7.89 7.71 7.69 7.53 7.52 7.47 7.45 7.44 7.43 7.42 7.40 7.40 7.37 7.36 7.35 7.32 7.31 7.29 7.27 7.19 7.18 7.17 7.15 7.14 7.09 7.09 7.07 7.06 7.05 7.03 7.02 6.97 6.95 5.64 5.64 5.63 5.63 5.46 5.45 4.52 4.51 4.51 4.50 2.78 2.77
Ph
N
N
O
F
HN
H
Bz
H
Ph
O
O
1.92 1.02 0.97 1.01 2.01 5.09 1.12 4.00 3.08 4.05 1.98 1.03 1.01 1.00 1.02
f1 (ppm)
195.56 173.09 170.97 165.77 163.26 154.88 147.22 137.04 136.30 134.99 133.62 131.63 130.67 130.29 130.10 129.67 129.59 128.76 128.66 128.49 128.32 128.24 128.23 127.96 127.84 127.74 126.16 125.76 125.72 125.54 125.25 124.61 119.07 118.86 116.47 116.25 72.01 65.74 55.99 47.19
f1 (ppm)

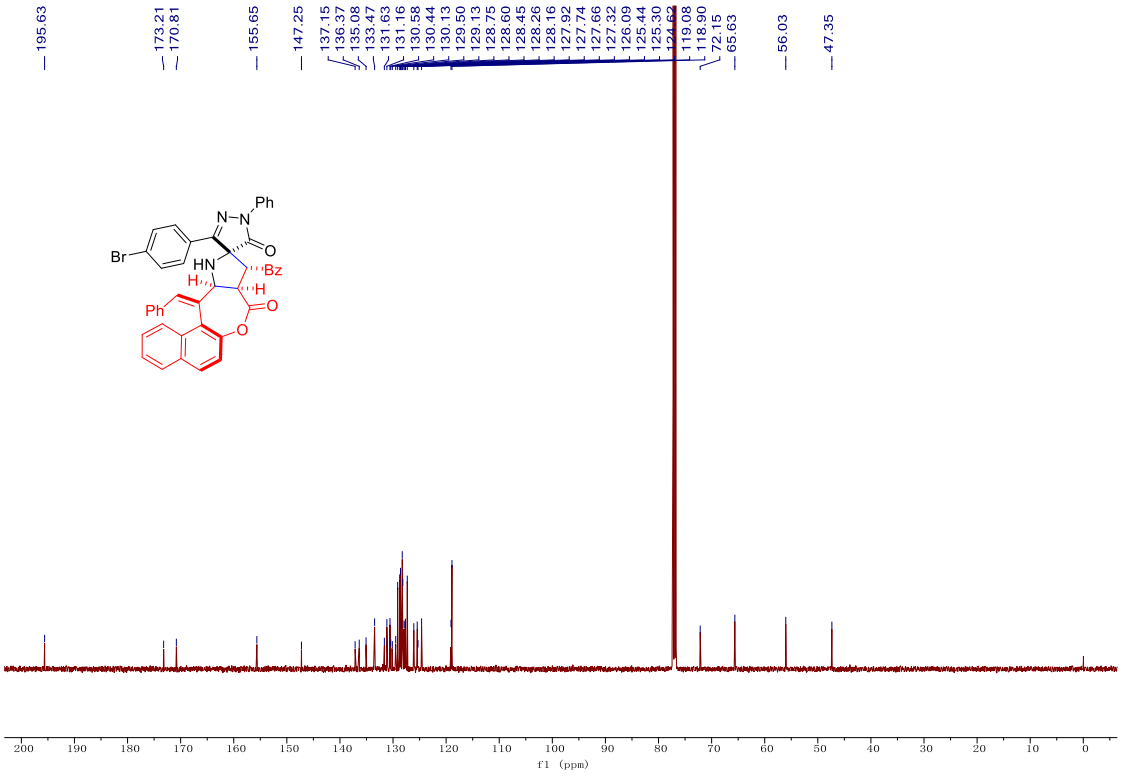
3ac


8.39
8.38
8.37
8.37
7.96
7.94
7.90
7.88
7.70
7.68
7.61
7.60
7.59
7.54
7.52
7.46
7.44
7.41
7.39
7.37
7.34
7.33
7.31
7.29
7.27
7.26
7.18
7.16
7.14
7.12
7.05
7.04
7.02
7.00
6.99
6.96
6.95
5.64
5.63
5.63
5.62
5.61
5.61
5.60
5.60
5.51
5.50
4.54
4.53
4.52
4.50
2.77
2.76
1.56



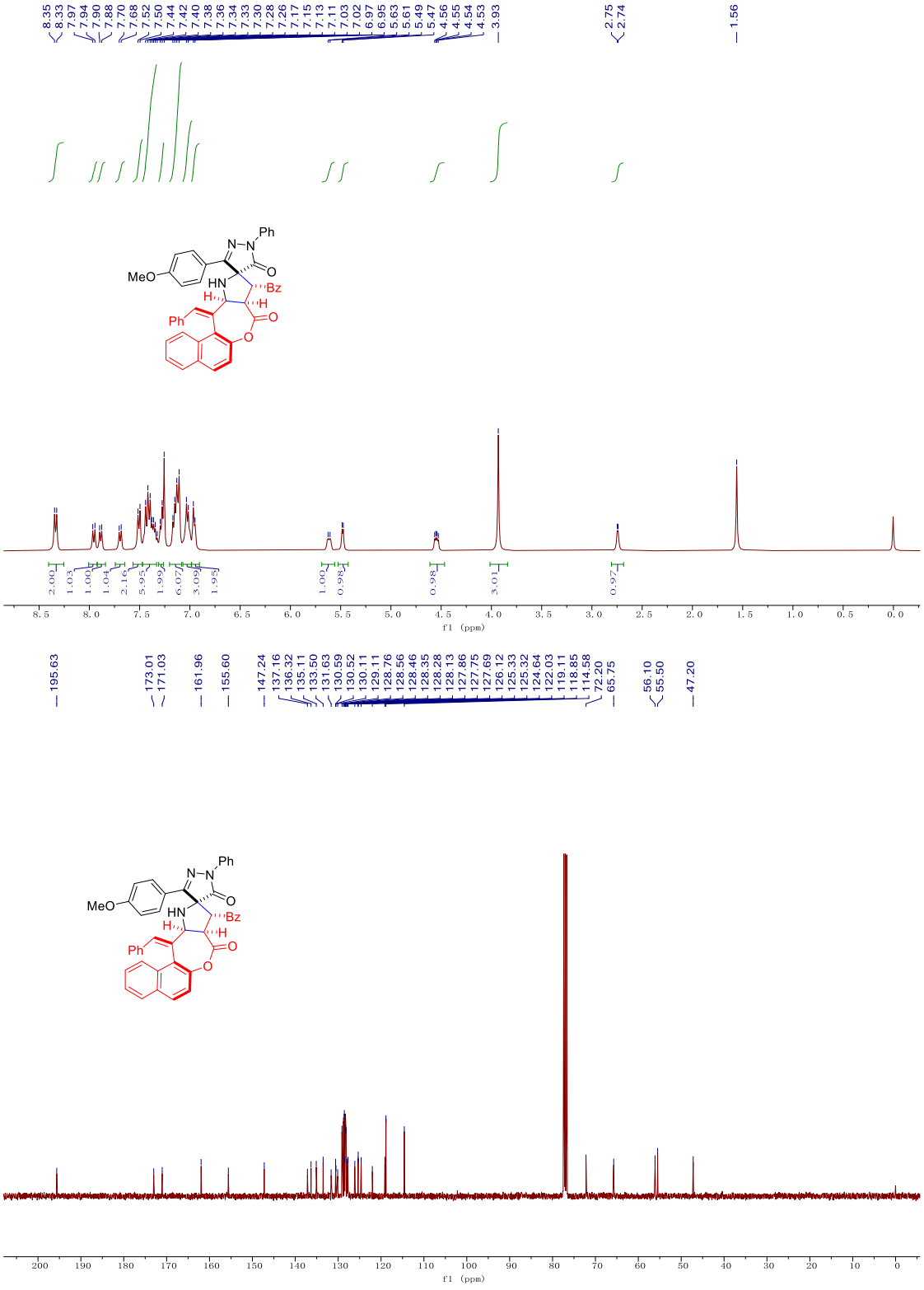
Ph
N
N
O
Br
HN
H
Bz
H
Ph
O
O


1.97
1.03
1.00
1.04
2.96
1.98
4.18
1.15
2.09
4.00
3.05
1.96
1.00
0.98
0.98
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

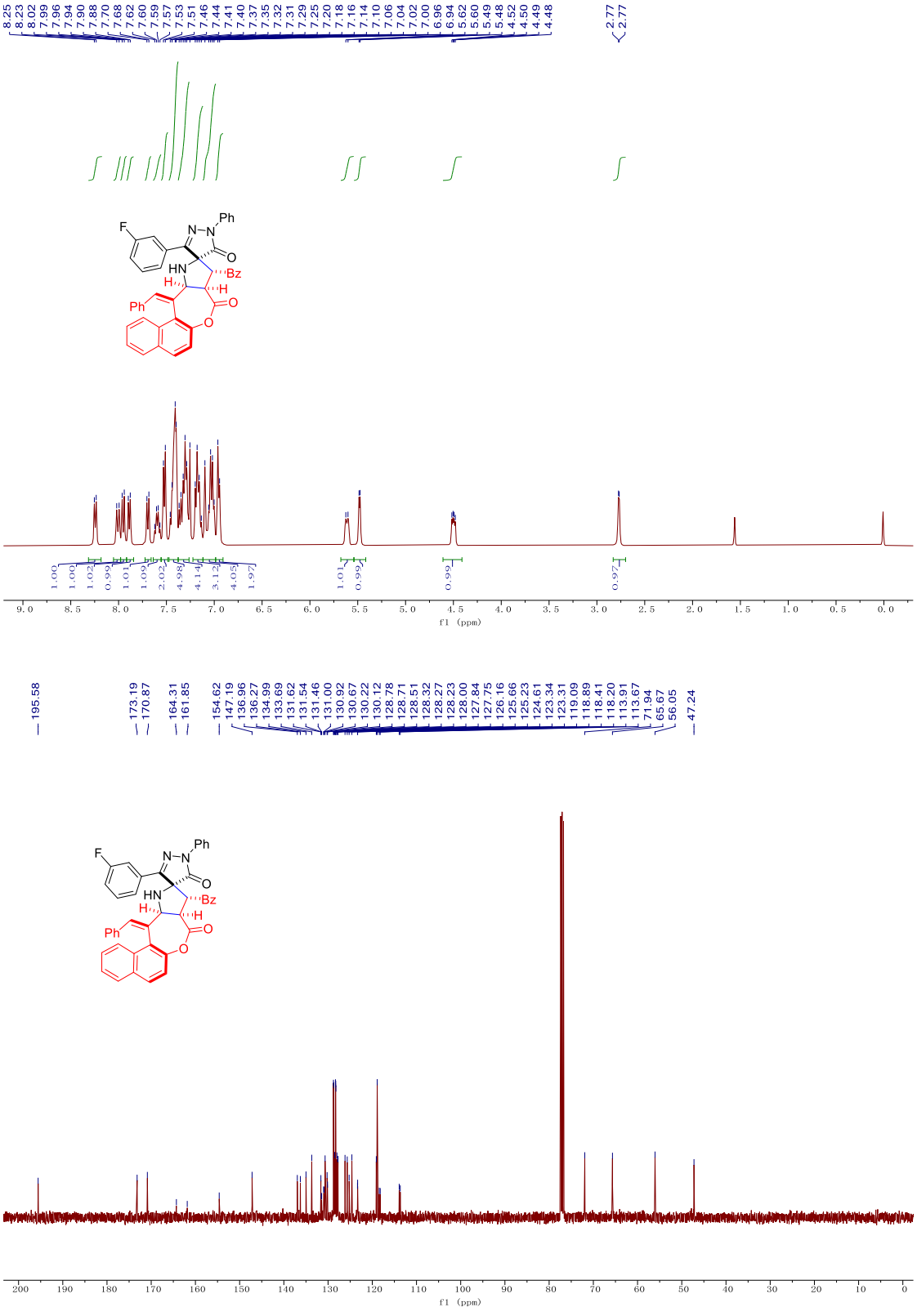

195.63
173.21
170.81
155.65
147.25
137.15
136.37
135.08
133.47
131.63
131.16
130.58
130.44
130.13
129.50
129.13
128.75
128.60
128.45
128.26
128.16
127.92
127.74
127.66
127.32
126.09
125.44
125.30
124.62
119.08
118.90
72.15
65.63
56.03
47.35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Ph
N
N
O
Br
HN
H
Bz
H
Ph
O
O

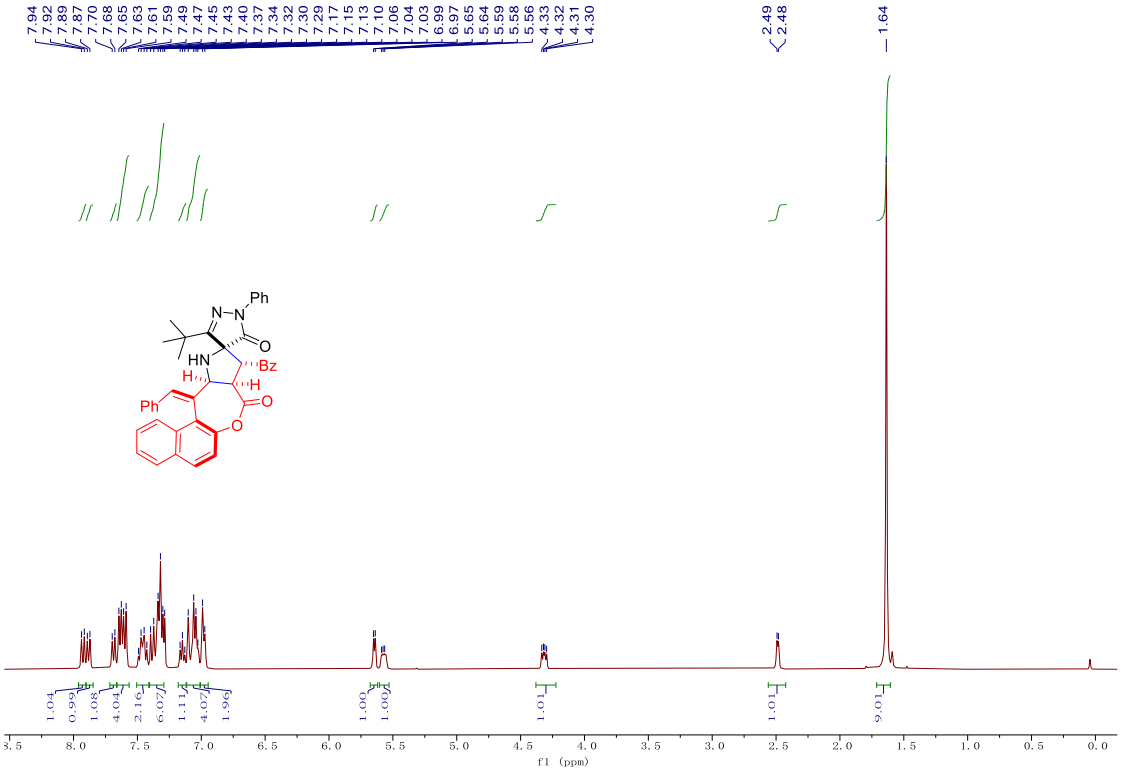
3ad

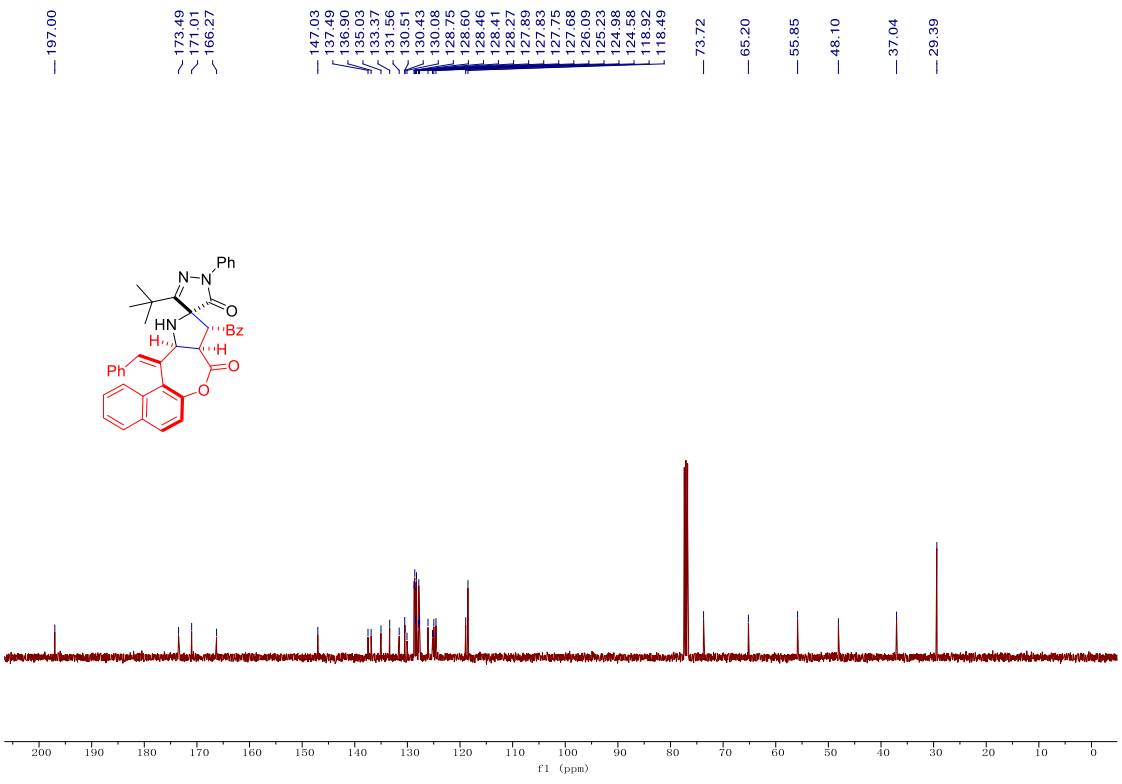

8.35
8.33
7.97
7.94
7.90
7.88
7.70
7.68
7.52
7.50
7.44
7.42
7.40
7.38
7.36
7.34
7.33
7.30
7.28
7.26
7.17
7.15
7.13
7.11
7.03
7.02
6.97
6.95
5.63
5.61
5.49
5.47
4.56
4.55
4.54
4.53
3.93
2.75
2.74
1.56
MeO
HN
Ph
N
N
O
H
Bz
H
Ph
O
O
2.00
1.03
1.00
1.04
2.16
5.95
1.99
6.07
3.09
1.95
1.00
0.98
0.98
3.01
0.97
f1 (ppm)
195.63
173.01
171.03
161.96
155.60
147.24
137.16
136.32
135.11
133.50
131.63
130.59
130.52
130.11
129.11
128.76
128.56
128.46
128.35
128.28
128.13
127.86
127.75
127.69
126.12
125.33
125.32
124.64
122.03
119.11
118.85
114.58
72.20
65.75
56.10
55.50
47.20
f1 (ppm)

3ae

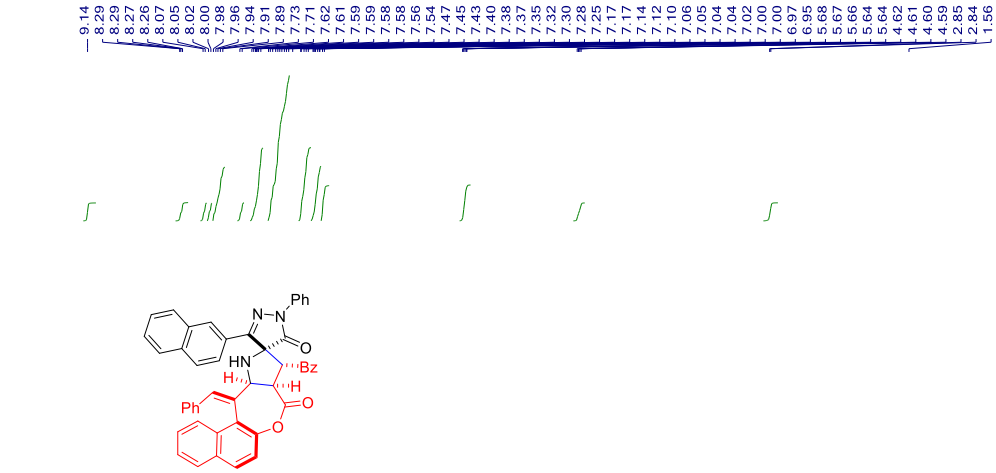

8.25
8.23
8.02
7.99
7.96
7.94
7.90
7.88
7.70
7.68
7.62
7.60
7.59
7.57
7.53
7.51
7.46
7.44
7.41
7.40
7.37
7.35
7.32
7.31
7.29
7.25
7.20
7.18
7.16
7.14
7.10
7.06
7.04
7.02
7.00
6.96
6.94
5.62
5.60
5.49
5.48
4.52
4.50
4.49
4.48
2.77
2.77
F
N
N
Ph
O
HN
H
Bz
H
Ph
O
O
1.00
1.00
1.02
0.99
1.01
1.09
2.02
4.98
4.14
3.12
4.05
1.97
1.01
0.99
0.99
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
195.58
173.19
170.87
164.31
161.85
154.62
147.19
136.96
136.27
134.99
133.69
131.62
131.54
131.46
131.00
130.92
130.67
130.22
130.12
128.78
128.71
128.51
128.32
128.27
128.23
128.00
127.84
127.75
126.16
125.66
125.23
124.61
123.34
123.31
119.09
118.89
118.41
118.20
113.91
113.67
71.94
65.67
56.05
47.24
F
N
N
Ph
O
HN
H
Bz
H
Ph
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3af

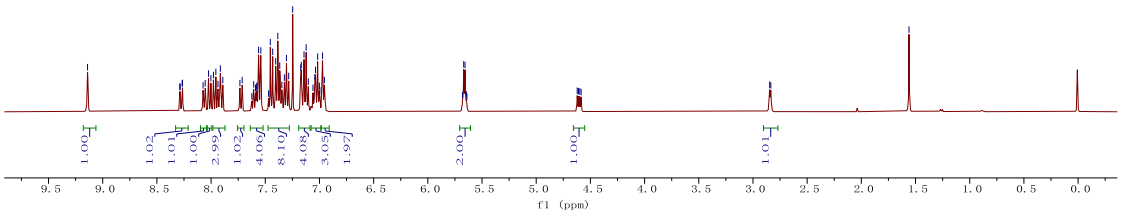

7.94
7.92
7.89
7.87
7.70
7.68
7.65
7.63
7.61
7.59
7.49
7.47
7.45
7.43
7.40
7.37
7.34
7.32
7.30
7.29
7.17
7.15
7.13
7.10
7.06
7.04
7.03
6.99
6.97
5.65
5.64
5.59
5.58
5.56
4.33
4.32
4.31
4.30
2.49
2.48
1.64
Ph
N
N
O
HN
H
Bz
H
O
Ph
O
1.04
0.93
1.08
4.04
2.16
6.07
1.11
4.07
1.96
1.00
1.00
1.01
1.01
9.01
f1 (ppm)


197.00
173.49
171.01
166.27
147.03
137.49
136.90
135.03
133.37
131.56
130.51
130.43
130.08
128.75
128.60
128.46
128.41
128.27
127.89
127.83
127.75
127.68
126.09
125.23
124.98
124.58
118.92
118.49
73.72
65.20
55.85
48.10
37.04
29.39
Ph
N
N
O
HN
H
Bz
H
Ph
O
O
f1 (ppm)

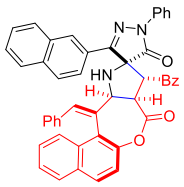
3ag

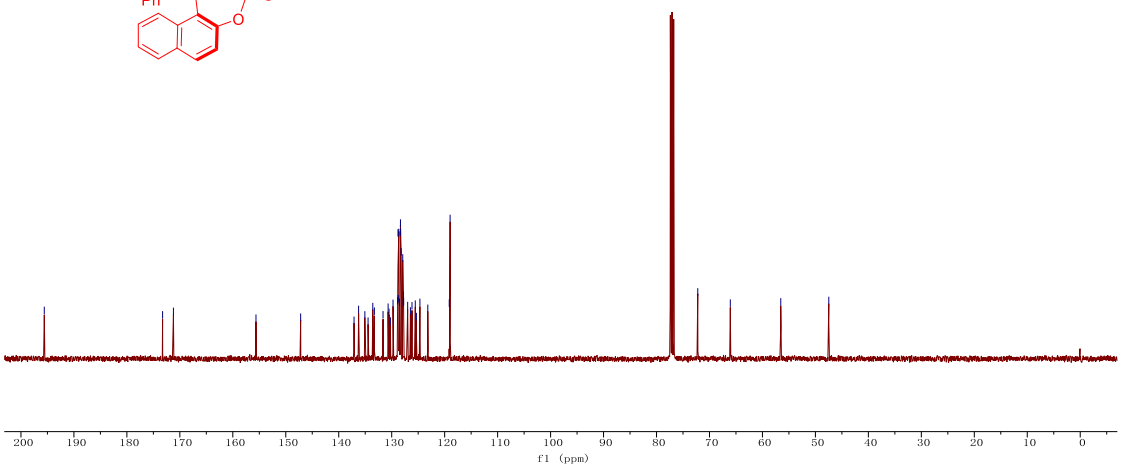

9.14
8.29
8.29
8.27
8.26
8.07
8.05
8.02
8.00
7.98
7.96
7.94
7.91
7.89
7.73
7.71
7.62
7.61
7.59
7.59
7.58
7.58
7.56
7.54
7.47
7.45
7.43
7.40
7.38
7.37
7.35
7.32
7.30
7.28
7.25
7.17
7.17
7.14
7.12
7.10
7.06
7.05
7.04
7.04
7.02
7.00
7.00
6.97
6.95
5.68
5.67
5.66
5.64
5.64
4.62
4.61
4.60
4.59
2.85
2.84
1.56

N
N
Ph
O
HN
H
Bz
H
Ph
O
O

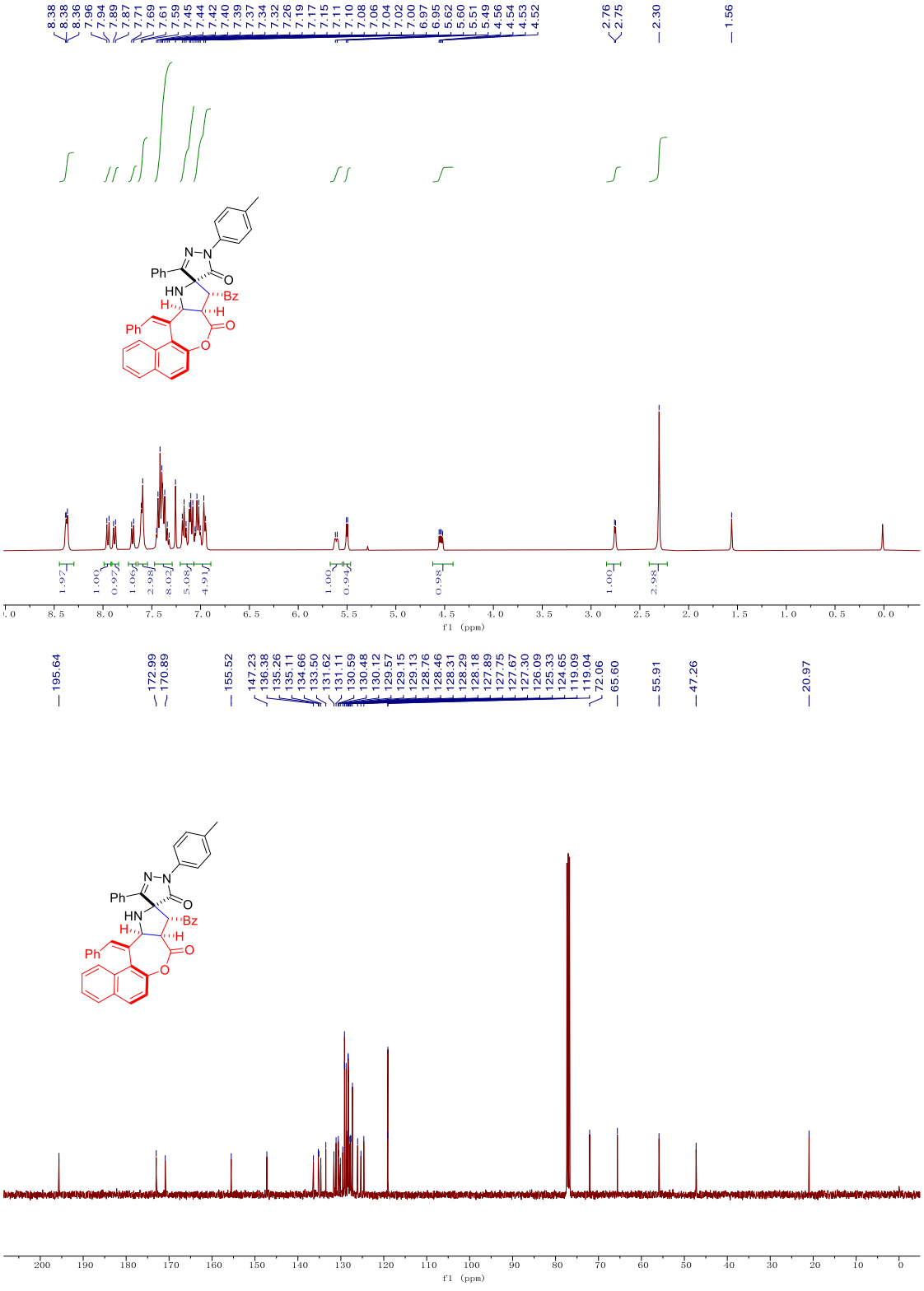

1.00
1.02
1.01
1.00
2.99
1.02
4.06
8.10
4.08
3.05
1.97
2.00
1.00
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


195.59
173.26
171.21
155.63
147.19
137.11
136.25
135.07
134.46
133.57
133.27
131.64
130.68
130.50
130.24
129.75
128.89
128.81
128.76
128.66
128.53
128.35
128.33
128.21
127.92
127.82
127.77
127.74
126.99
126.47
126.17
125.55
125.34
124.67
123.18
119.14
118.97
72.21
66.07
56.54
47.47

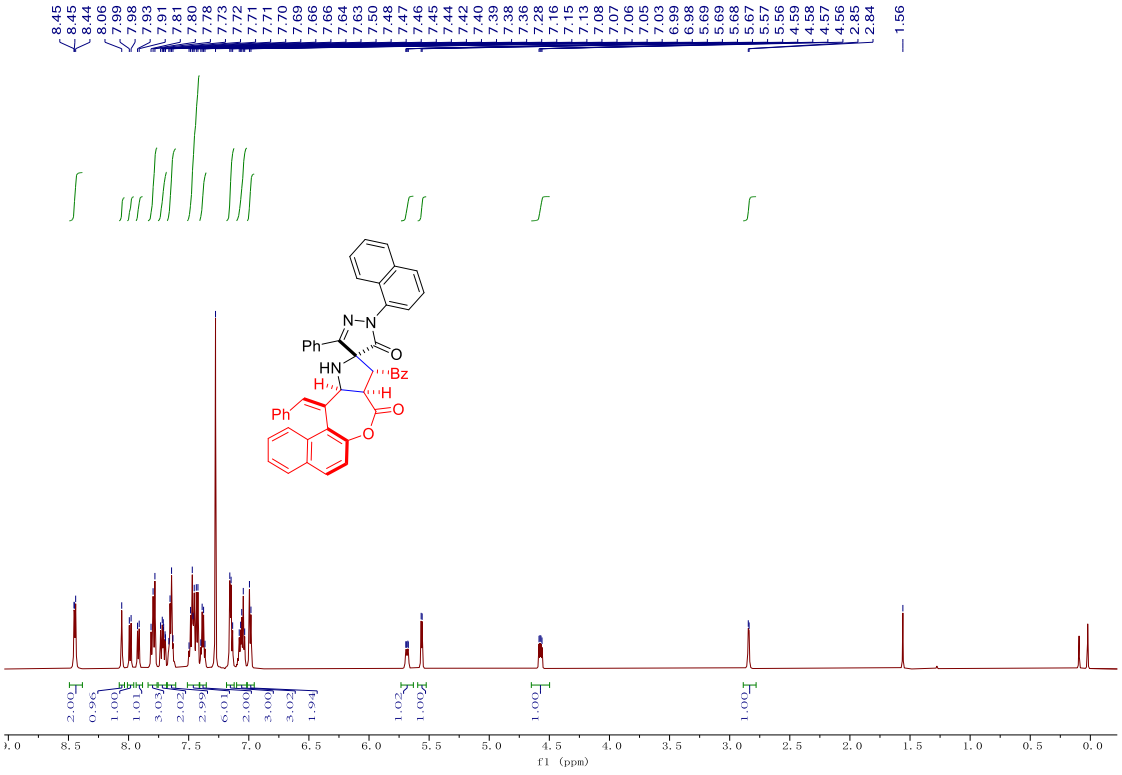

N
N
Ph
O
HN
H
Bz
H
Ph
O
O

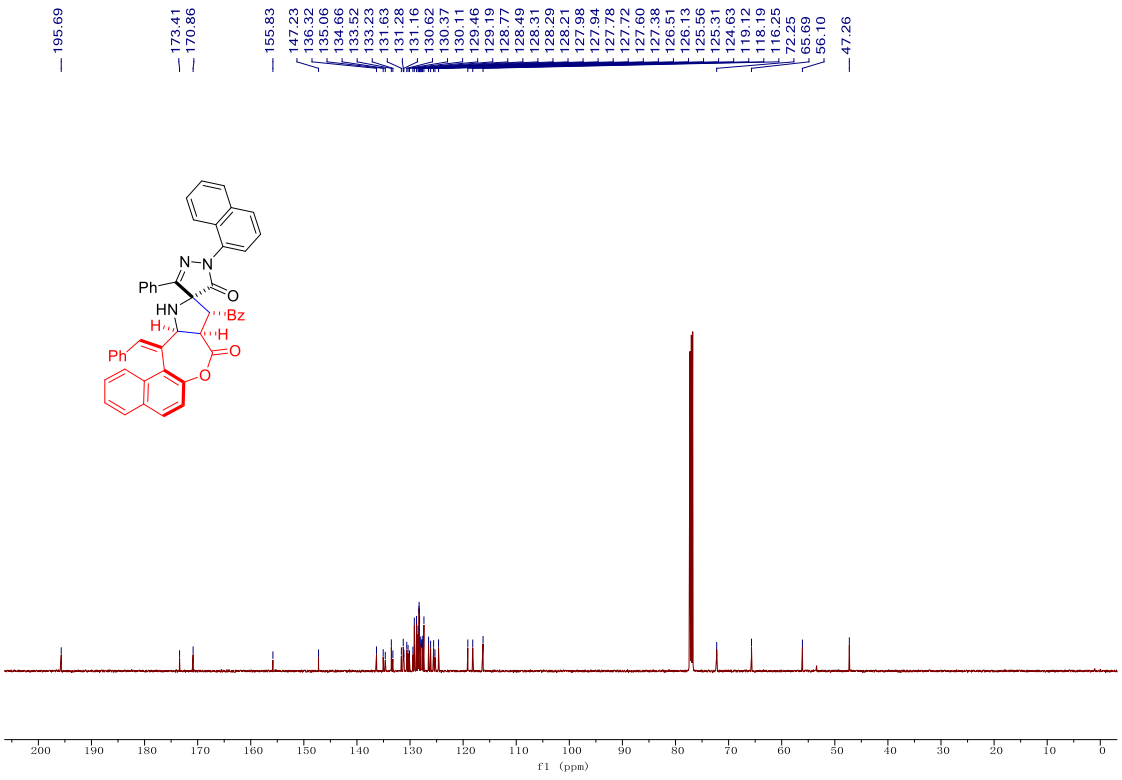

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ah

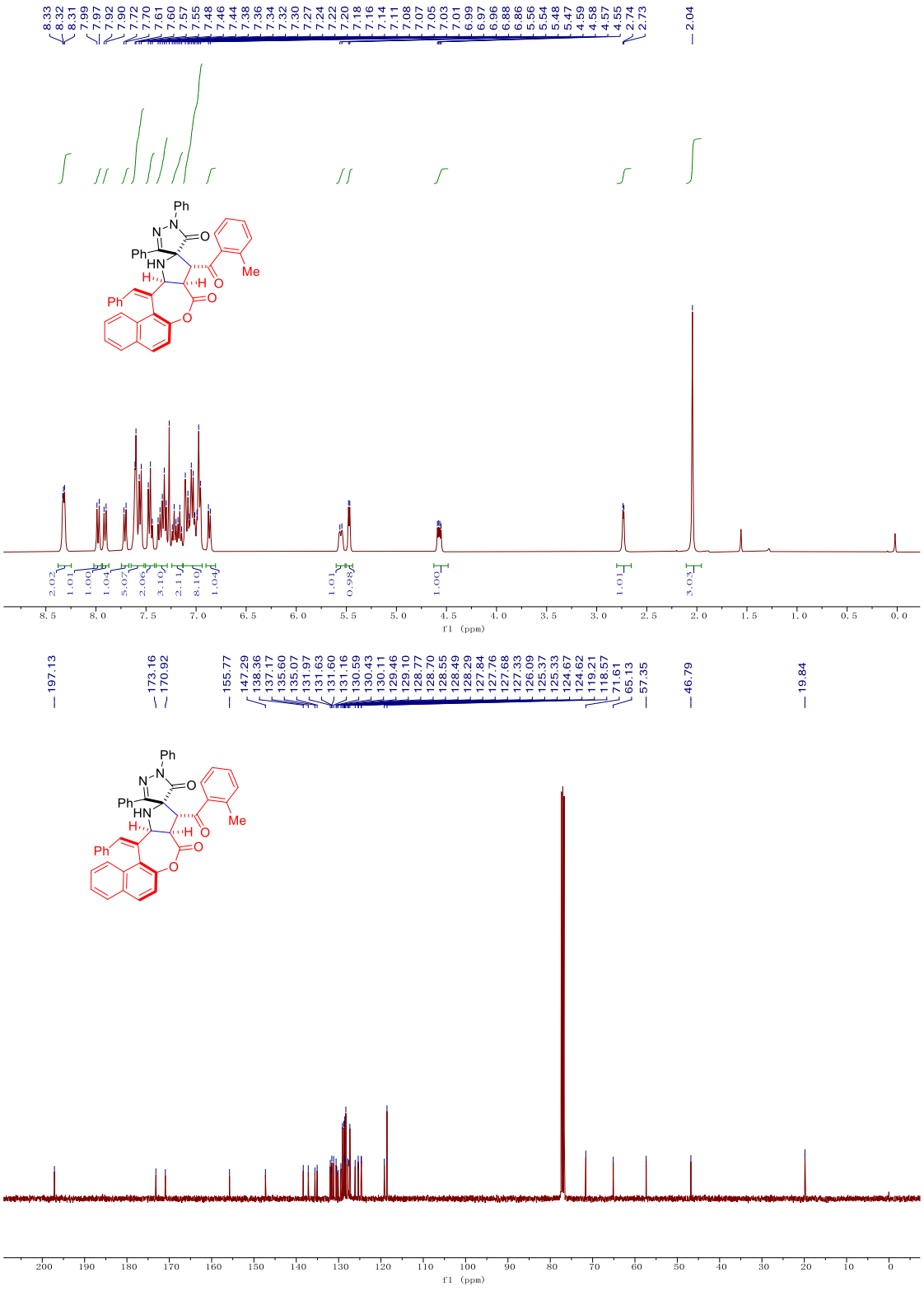

8.38
8.38
8.36
7.96
7.94
7.89
7.87
7.71
7.69
7.61
7.59
7.45
7.44
7.42
7.40
7.39
7.37
7.34
7.32
7.26
7.19
7.17
7.15
7.11
7.10
7.08
7.06
7.04
7.02
7.00
6.97
6.95
5.62
5.60
5.51
5.49
4.56
4.54
4.53
4.52
2.76
2.75
2.30
1.56
Ph
N
N
O
HN
H
Bz
H
Ph
O
O
1.97
1.00
0.97
1.06
2.98
8.02
5.08
4.91
1.00
0.94
0.98
1.00
2.98
f1 (ppm)
195.64
172.99
170.89
155.52
147.23
136.38
135.26
135.11
134.66
133.50
131.62
131.11
130.59
130.48
130.12
129.57
129.15
129.13
128.76
128.46
128.31
128.29
128.18
127.89
127.75
127.67
127.30
126.09
125.33
124.65
119.09
119.04
72.06
65.60
55.91
47.26
20.97
f1 (ppm)

3ai

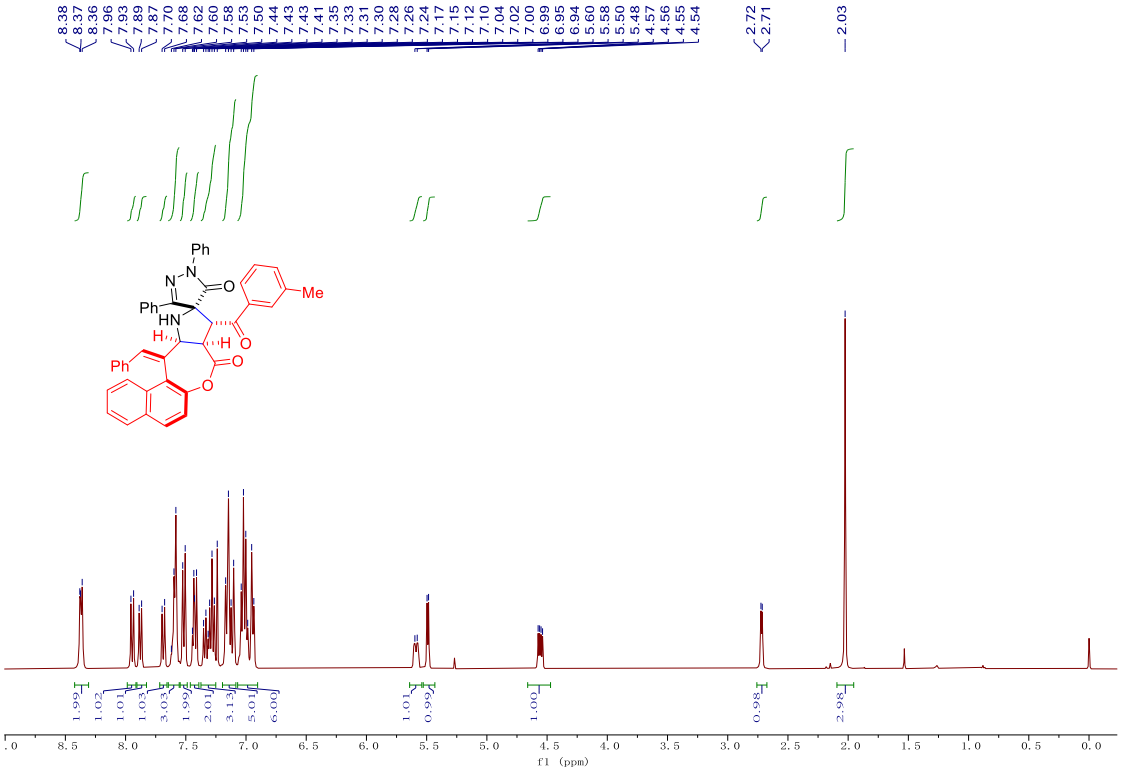

8.45
8.45
8.44
8.06
7.99
7.98
7.93
7.91
7.81
7.80
7.78
7.73
7.72
7.71
7.71
7.70
7.69
7.66
7.66
7.64
7.63
7.50
7.48
7.47
7.46
7.45
7.44
7.42
7.40
7.39
7.38
7.36
7.28
7.16
7.15
7.13
7.08
7.07
7.06
7.05
7.03
6.99
6.98
5.69
5.69
5.68
5.67
5.57
5.56
4.59
4.58
4.57
4.56
2.85
2.84
1.56
N
N
Ph
O
HN
H
Bz
H
Ph
O
O
2.00
0.96
1.00
1.01
3.03
2.02
2.92
6.01
2.00
3.09
3.02
1.94
1.02
1.02
1.00
1.00
f1 (ppm)

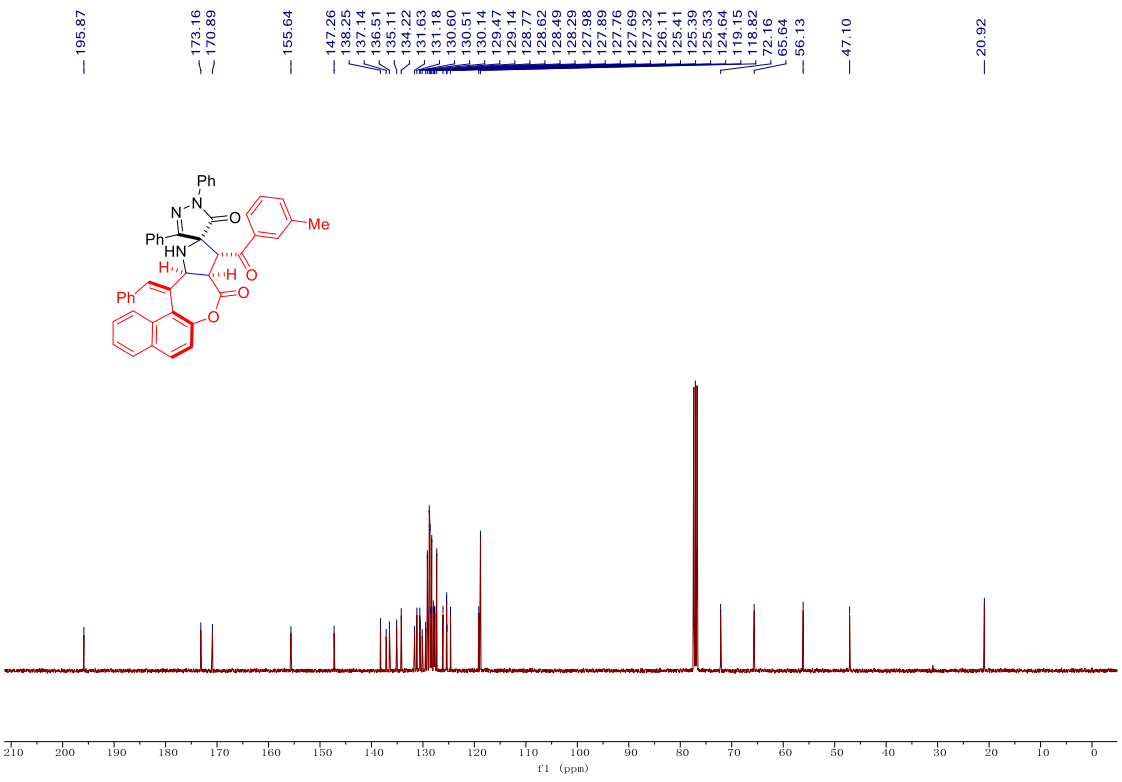

195.69
173.41
170.86
155.83
147.23
136.32
135.06
134.66
133.52
133.23
131.63
131.28
131.16
130.62
130.37
130.11
129.46
129.19
128.77
128.49
128.31
128.29
128.21
127.98
127.94
127.78
127.72
127.60
127.38
126.51
126.13
125.56
125.31
124.63
119.12
118.19
116.25
72.25
65.69
56.10
47.26
N
N
Ph
O
HN
H
Bz
H
Ph
O
O
f1 (ppm)

3ba

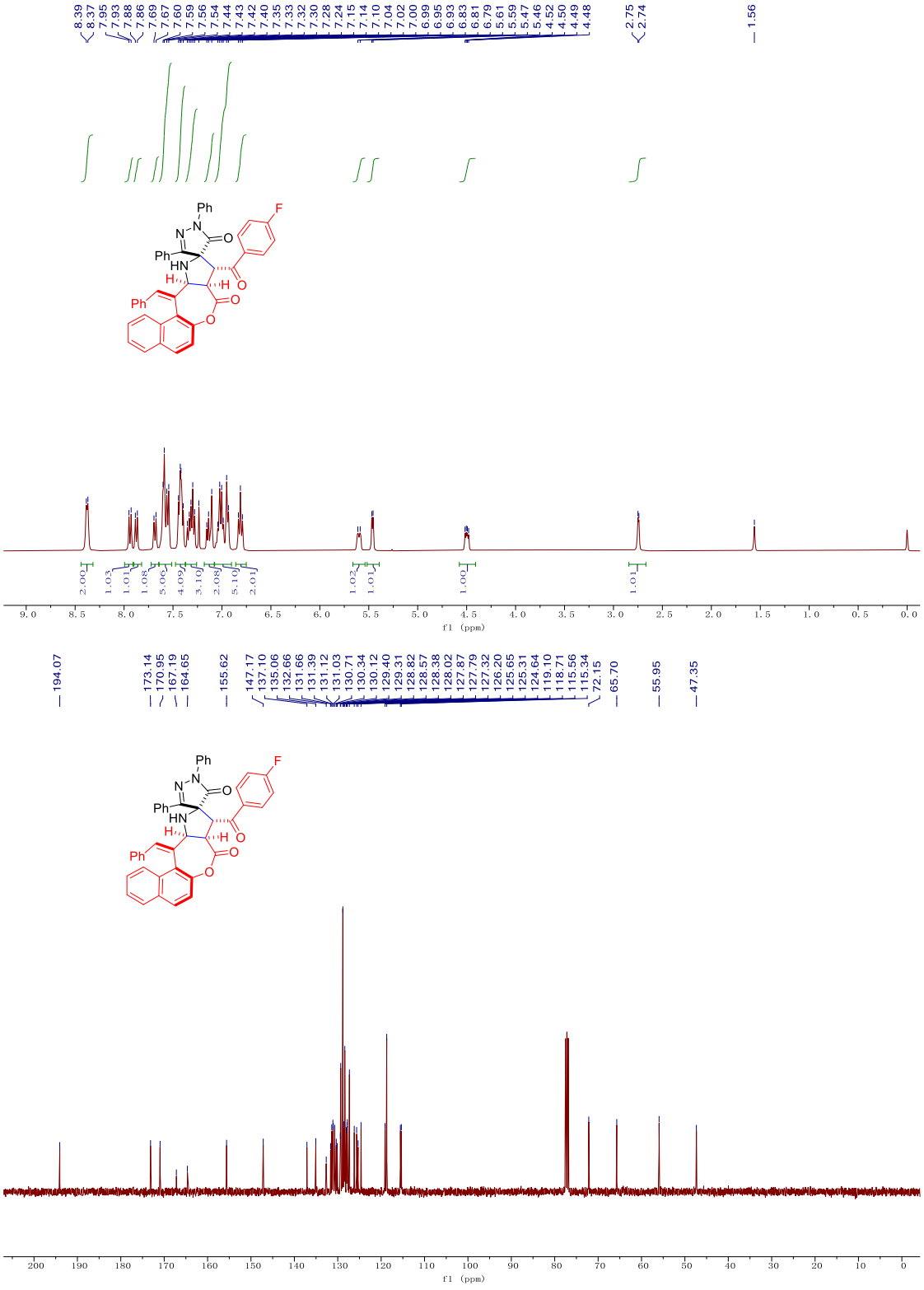

8.33
8.32
8.31
7.99
7.97
7.92
7.90
7.72
7.70
7.61
7.60
7.57
7.55
7.48
7.46
7.44
7.38
7.36
7.34
7.32
7.30
7.27
7.24
7.22
7.20
7.18
7.16
7.14
7.11
7.08
7.07
7.05
7.03
7.01
6.99
6.97
6.96
6.88
6.86
5.56
5.54
5.48
5.47
4.59
4.58
4.57
4.55
2.74
2.73
2.04
Ph
N
N
O
Ph
HN
H
H
O
Me
Ph
O
O
2.03
1.01
1.06
1.04
5.07
2.06
3.10
2.11
8.10
1.04
1.01
0.98
1.00
1.01
3.03
f1 (ppm)
197.13
173.16
170.92
155.77
147.29
138.36
137.17
135.60
135.07
131.97
131.63
131.60
131.16
130.59
130.43
130.11
129.46
129.10
128.77
128.70
128.55
128.49
128.29
127.84
127.76
127.68
127.33
126.09
125.37
125.33
124.67
124.62
119.21
118.57
71.61
65.13
57.35
46.79
19.84
f1 (ppm)

3ca


8.38
8.37
8.36
7.96
7.93
7.89
7.87
7.70
7.68
7.62
7.60
7.58
7.53
7.50
7.44
7.43
7.43
7.41
7.35
7.33
7.31
7.30
7.28
7.26
7.24
7.17
7.15
7.12
7.10
7.04
7.02
7.00
6.99
6.95
6.94
5.60
5.58
5.50
5.48
4.57
4.56
4.55
4.54
2.72
2.71
2.03
Ph
N
N
O
Ph
HN
H
H
O
O
Ph
O
Me
1.92
1.02
1.01
1.03
3.03
1.99
2.01
3.13
5.01
6.00
1.01
0.99
1.00
0.98
2.98
f1 (ppm)

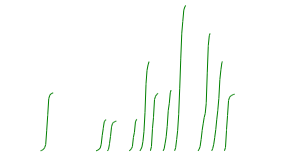

195.87
173.16
170.89
155.64
147.26
138.25
137.14
136.51
135.11
134.22
131.63
131.18
130.60
130.51
130.14
129.47
129.14
128.77
128.62
128.49
128.29
127.98
127.89
127.76
127.69
127.32
126.11
125.41
125.39
125.33
124.64
119.15
118.82
72.16
65.64
56.13
47.10
20.92
Ph
N
N
O
Ph
HN
H
H
O
O
Ph
O
Me
f1 (ppm)

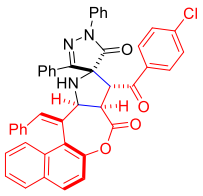
3da

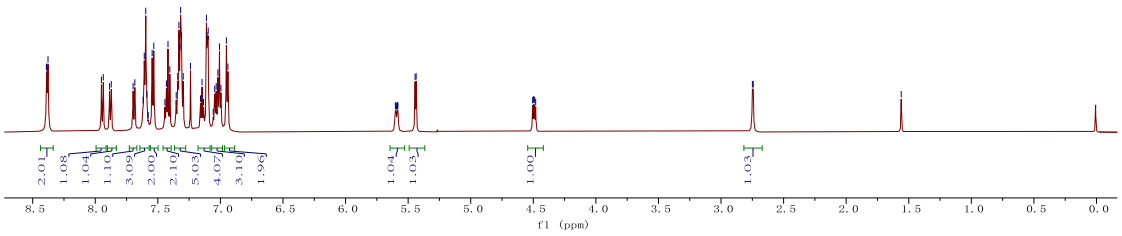

8.39
8.37
7.95
7.93
7.88
7.86
7.69
7.67
7.60
7.59
7.56
7.54
7.44
7.43
7.42
7.40
7.35
7.33
7.32
7.30
7.28
7.24
7.15
7.14
7.10
7.04
7.02
7.00
6.99
6.95
6.93
6.83
6.81
6.79
5.61
5.59
5.47
5.46
4.52
4.50
4.49
4.48
2.75
2.74
1.56
Ph
N
N
O
Ph
HN
H
H
O
O
Ph
O
F
2.00
1.03
1.01
1.08
5.06
4.09
3.10
2.08
5.10
2.01
1.02
1.01
1.00
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
194.07
173.14
170.95
167.19
164.65
155.62
147.17
137.10
135.06
132.66
131.66
131.39
131.12
131.03
130.71
130.34
130.12
129.40
129.31
128.82
128.57
128.38
128.02
127.87
127.79
127.32
126.20
125.65
125.31
124.64
119.10
118.71
115.56
115.34
72.15
65.70
55.95
47.35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

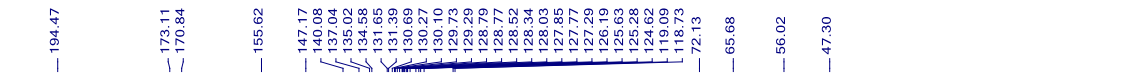
3ea

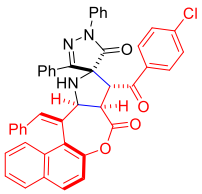

8.39
8.39
8.38
7.95
7.94
7.89
7.87
7.70
7.68
7.62
7.61
7.60
7.59
7.58
7.55
7.53
7.44
7.43
7.42
7.40
7.35
7.34
7.33
7.32
7.31
7.30
7.24
7.16
7.15
7.13
7.11
7.11
7.10
7.10
7.06
7.05
7.03
7.02
7.01
7.00
6.95
6.94
5.60
5.60
5.59
5.59
5.59
5.58
5.44
5.44
4.51
4.50
4.49
4.48
2.75
2.74
1.56




Ph
N
N
O
Ph
HN
H
H
O
Cl
O
Ph
O

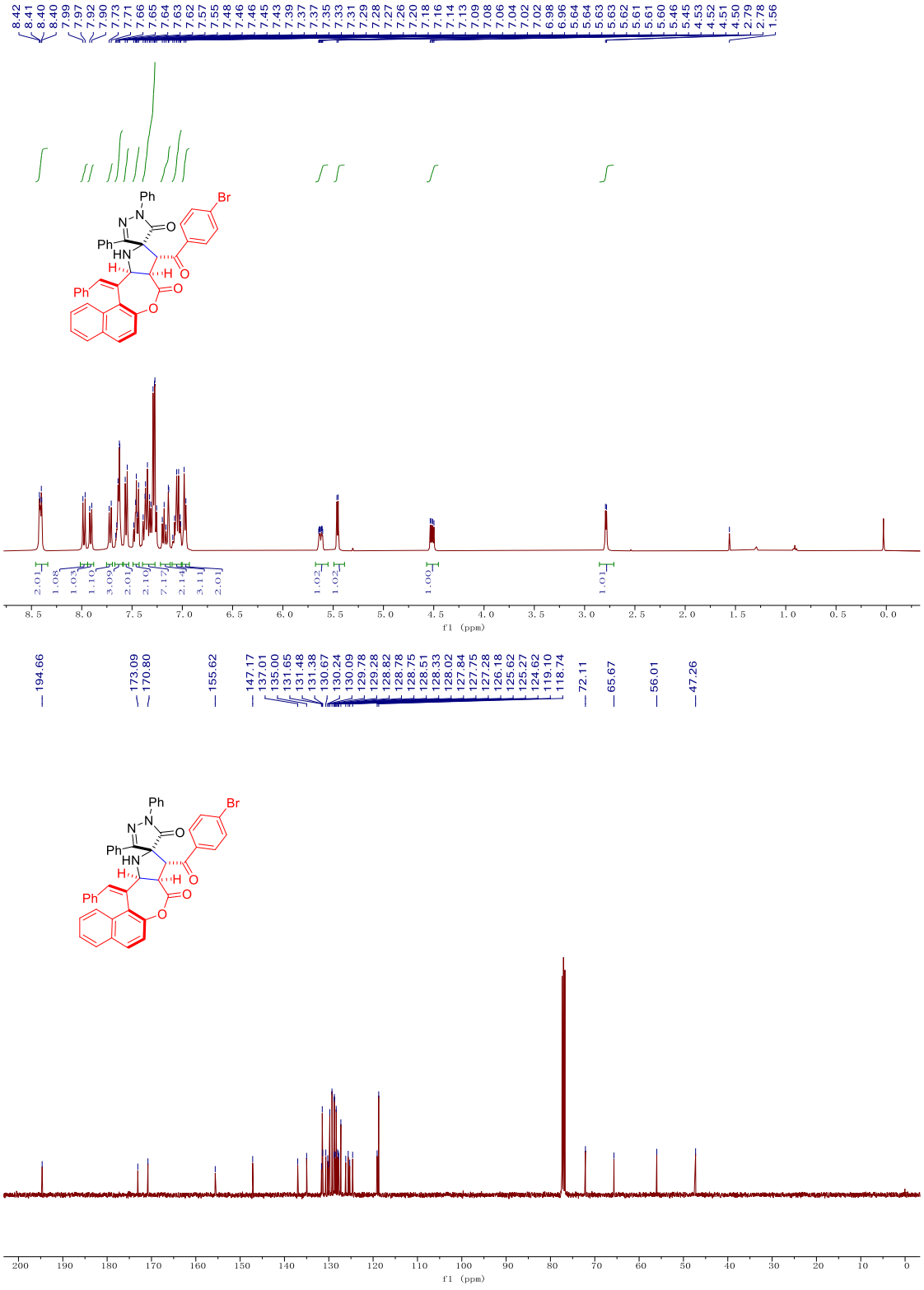

2.01
1.08
1.04
1.10
3.05
2.00
2.10
5.03
4.07
3.10
1.96
1.04
1.03
1.00
1.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.47
173.11
170.84
155.62
147.17
140.08
137.04
135.02
134.58
131.65
131.39
130.69
130.27
130.10
129.73
129.29
128.79
128.77
128.52
128.34
128.03
127.85
127.77
127.29
126.19
125.63
125.28
124.62
119.09
118.73
72.13
65.68
56.02
47.30

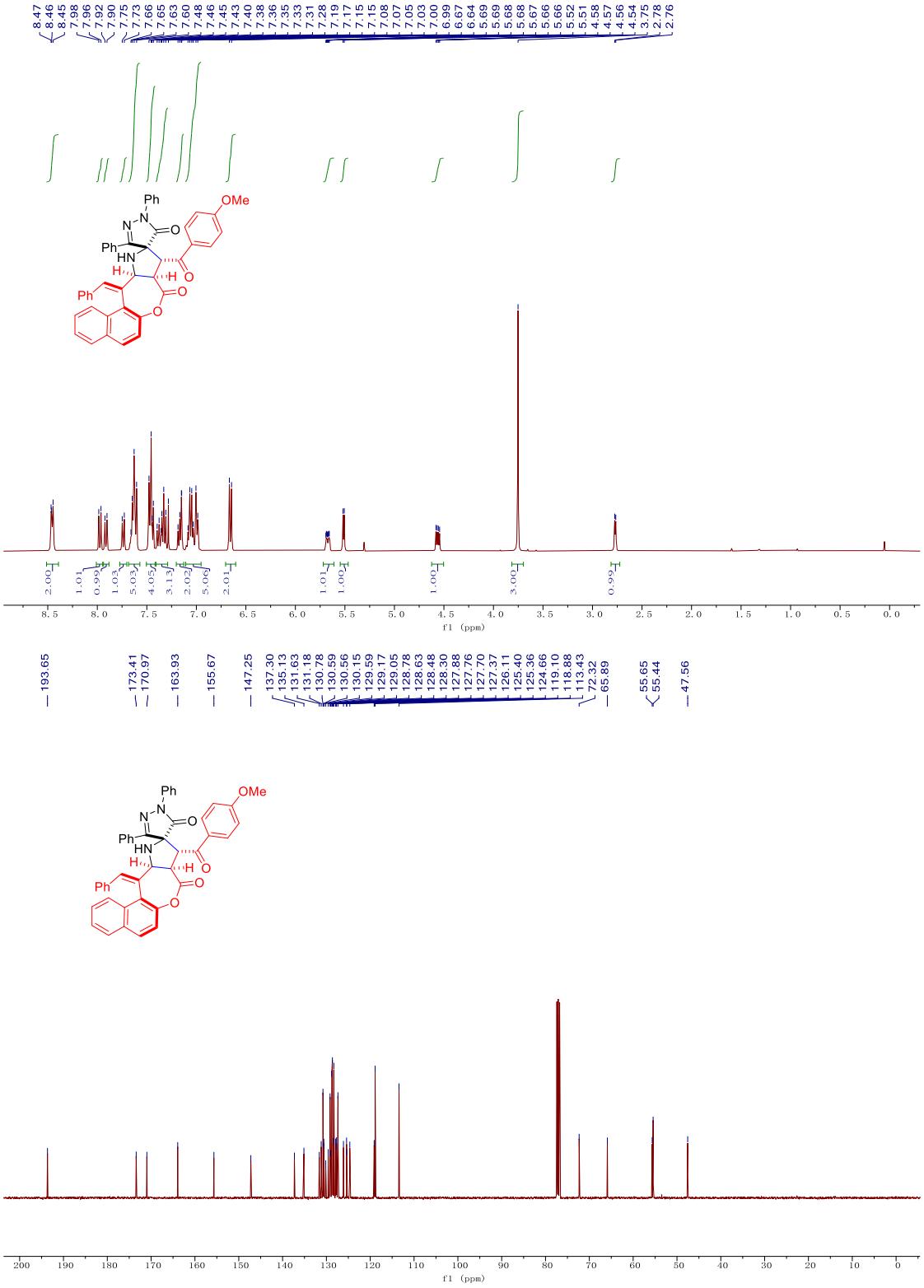

Ph
N
N
O
Ph
HN
H
H
O
Cl
O
Ph
O

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

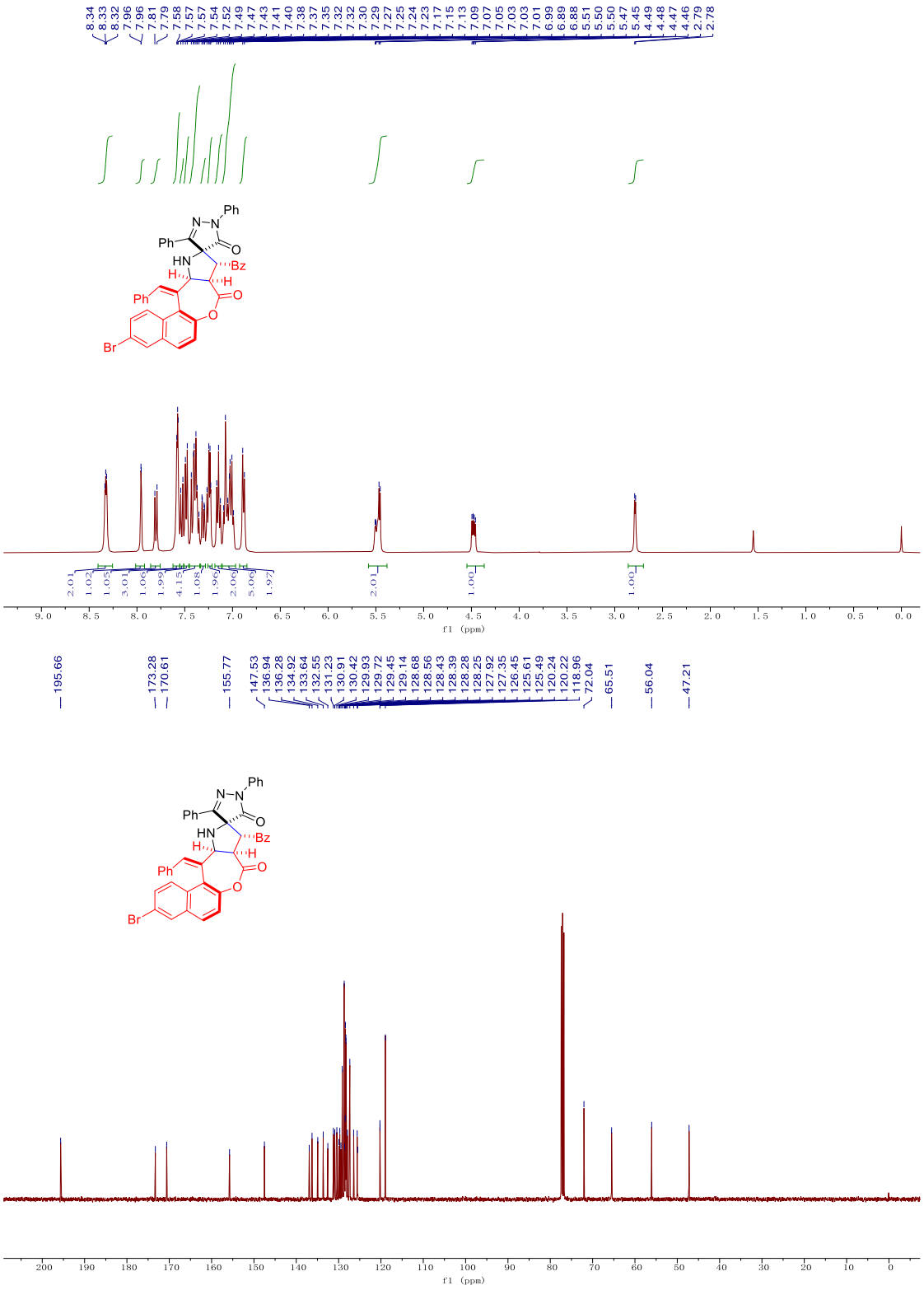
3fa


8.42 8.41 8.40 8.40 7.99 7.97 7.92 7.90 7.73 7.71 7.66 7.65 7.64 7.63 7.62 7.57 7.55 7.48 7.46 7.46 7.45 7.43 7.39 7.37 7.37 7.35 7.33 7.31 7.29 7.28 7.27 7.26 7.20 7.18 7.16 7.14 7.13 7.09 7.08 7.06 7.04 7.02 7.02 6.98 6.96 5.64 5.64 5.63 5.63 5.62 5.61 5.61 5.60 5.46 5.45 4.53 4.52 4.51 4.50 2.79 2.78 1.56
Ph
Br
N
O
Ph
HN
H
H
O
Ph
O
O
2.01 1.08 1.03 1.10 3.09 2.01 2.10 7.17 2.14 3.11 2.01 1.02 1.02 1.00 1.01
f1 (ppm)
194.66 173.09 170.80 155.62 147.17 137.01 135.00 131.65 131.48 131.38 130.67 130.24 130.09 129.78 129.28 128.82 128.78 128.75 128.51 128.33 128.02 127.84 127.75 127.28 126.18 125.62 125.27 124.62 119.10 118.74 72.11 65.67 56.01 47.26
f1 (ppm)

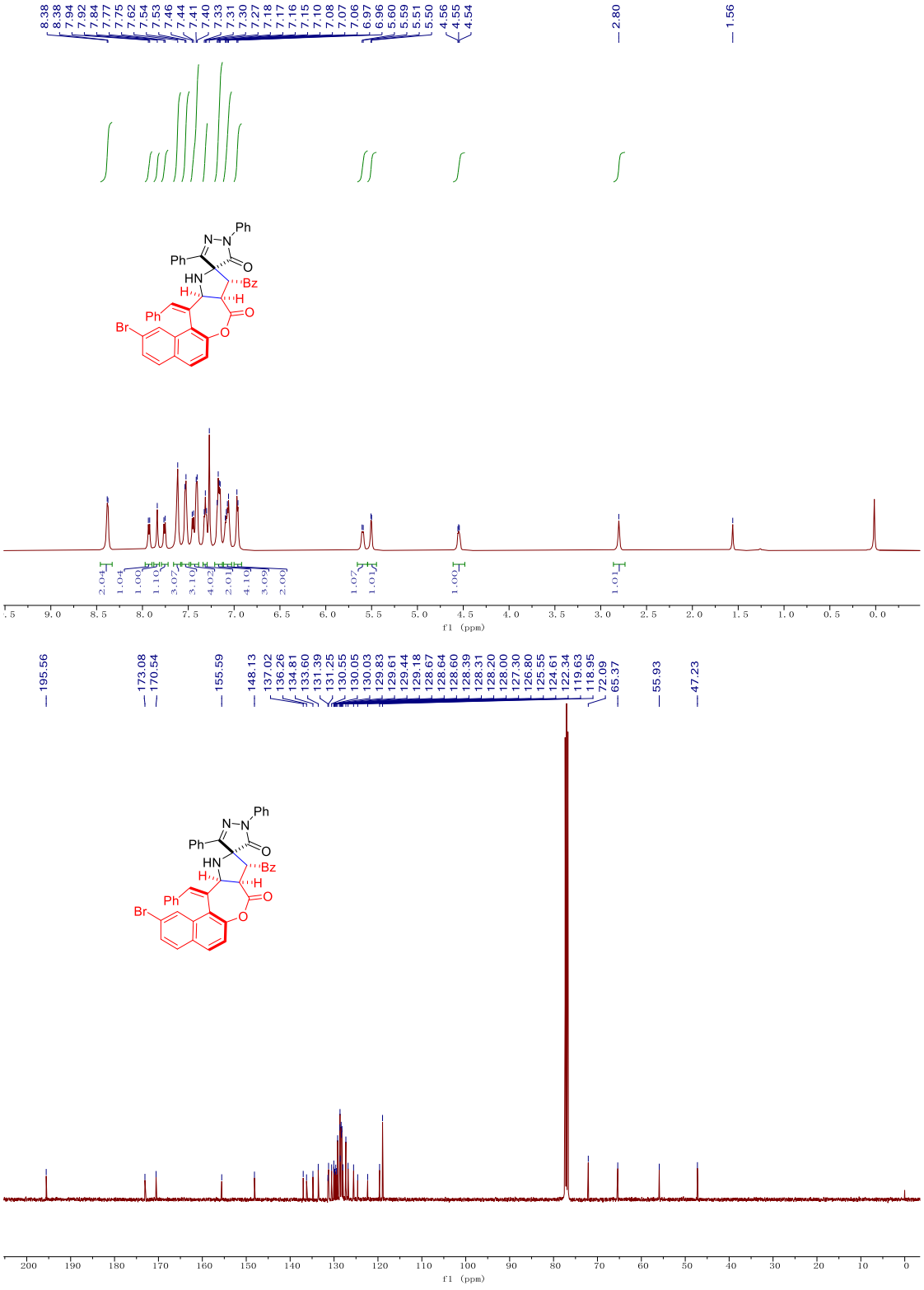
3ga


8.47 8.46 8.45 7.98 7.96 7.92 7.90 7.75 7.73 7.66 7.65 7.63 7.60 7.48 7.46 7.45 7.43 7.40 7.38 7.36 7.35 7.33 7.31 7.28 7.19 7.17 7.15 7.15 7.08 7.07 7.05 7.03 7.00 6.99 6.67 6.64 5.69 5.69 5.68 5.68 5.67 5.66 5.66 5.52 5.51 4.58 4.57 4.56 4.54 3.75 2.78 2.76
Ph
N
N
O
Ph
HN
H
H
O
O
Ph
O
OMe
2.00 1.01 0.99 1.03 5.03 4.05 3.13 2.02 5.06 2.01 1.01 1.00 1.00 3.00 0.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
193.65 173.41 170.97 163.93 155.67 147.25 137.30 135.13 131.63 131.18 130.78 130.59 130.56 130.15 129.59 129.17 129.05 128.78 128.63 128.48 128.30 127.88 127.76 127.70 127.37 126.11 125.40 125.36 124.66 119.10 118.88 113.43 72.32 65.89 55.65 55.44 47.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

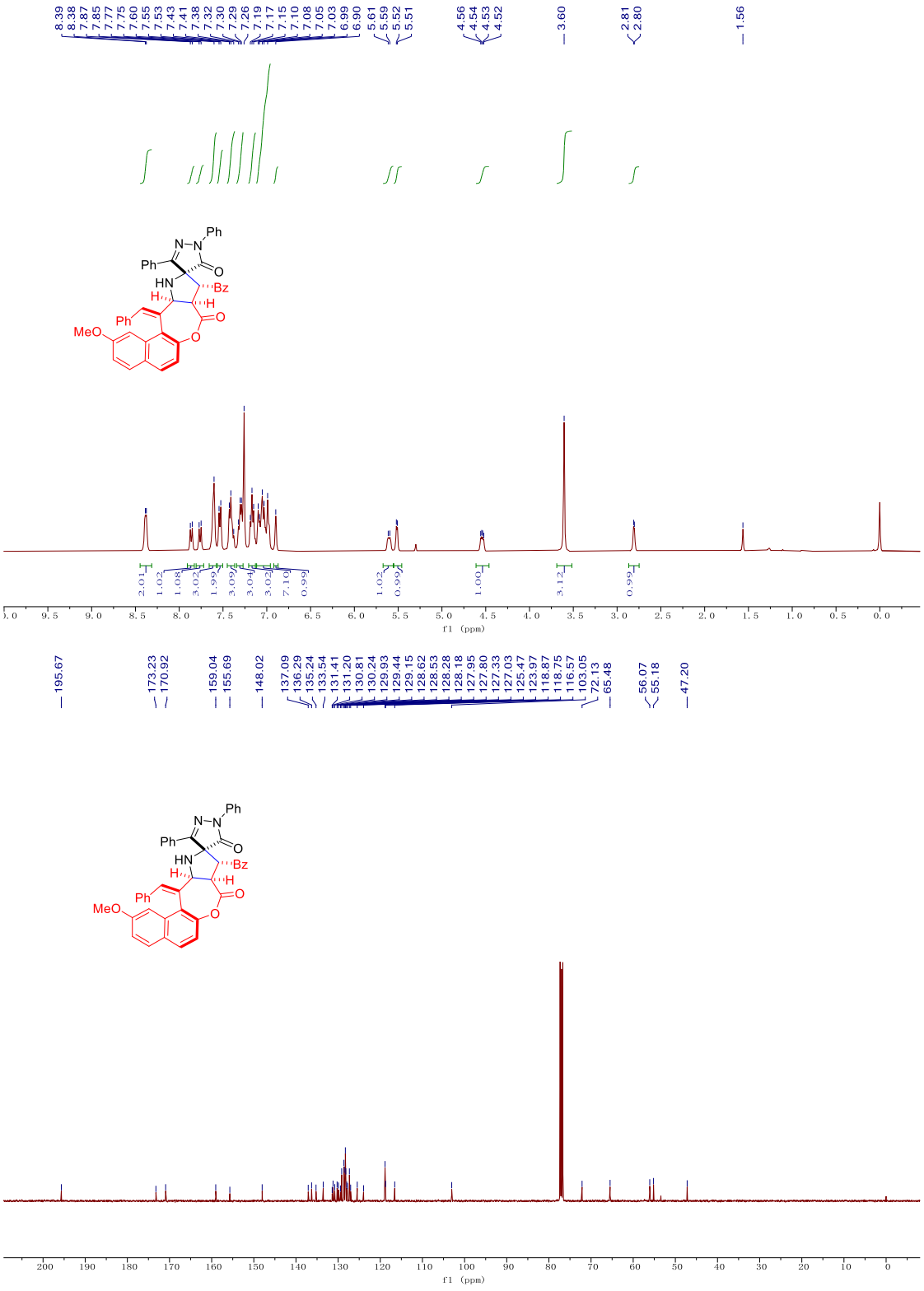
3ha


8.34 8.33 8.32 7.96 7.96 7.81 7.79 7.58 7.57 7.57 7.54 7.52 7.49 7.47 7.43 7.41 7.40 7.38 7.37 7.35 7.32 7.32 7.30 7.29 7.27 7.25 7.24 7.23 7.17 7.15 7.13 7.09 7.07 7.05 7.03 7.03 7.01 6.99 6.89 6.88 5.51 5.50 5.50 5.47 5.45 4.49 4.48 4.47 4.46 2.79 2.78
Ph
N–N
Ph
O
HN
H
Bz
H
Ph
O
O
Br
2.01 1.02 1.05 3.01 1.06 1.93 4.15 1.08 1.96 2.06 5.06 1.97 2.01 1.00 1.00
f1 (ppm)
195.66 173.28 170.61 155.77 147.53 136.94 136.28 134.92 133.64 132.55 131.23 130.91 130.42 129.93 129.72 129.45 129.14 128.68 128.56 128.43 128.39 128.28 128.25 127.92 127.35 126.45 125.61 125.49 120.24 120.22 118.96 72.04 65.51 56.04 47.21
f1 (ppm)

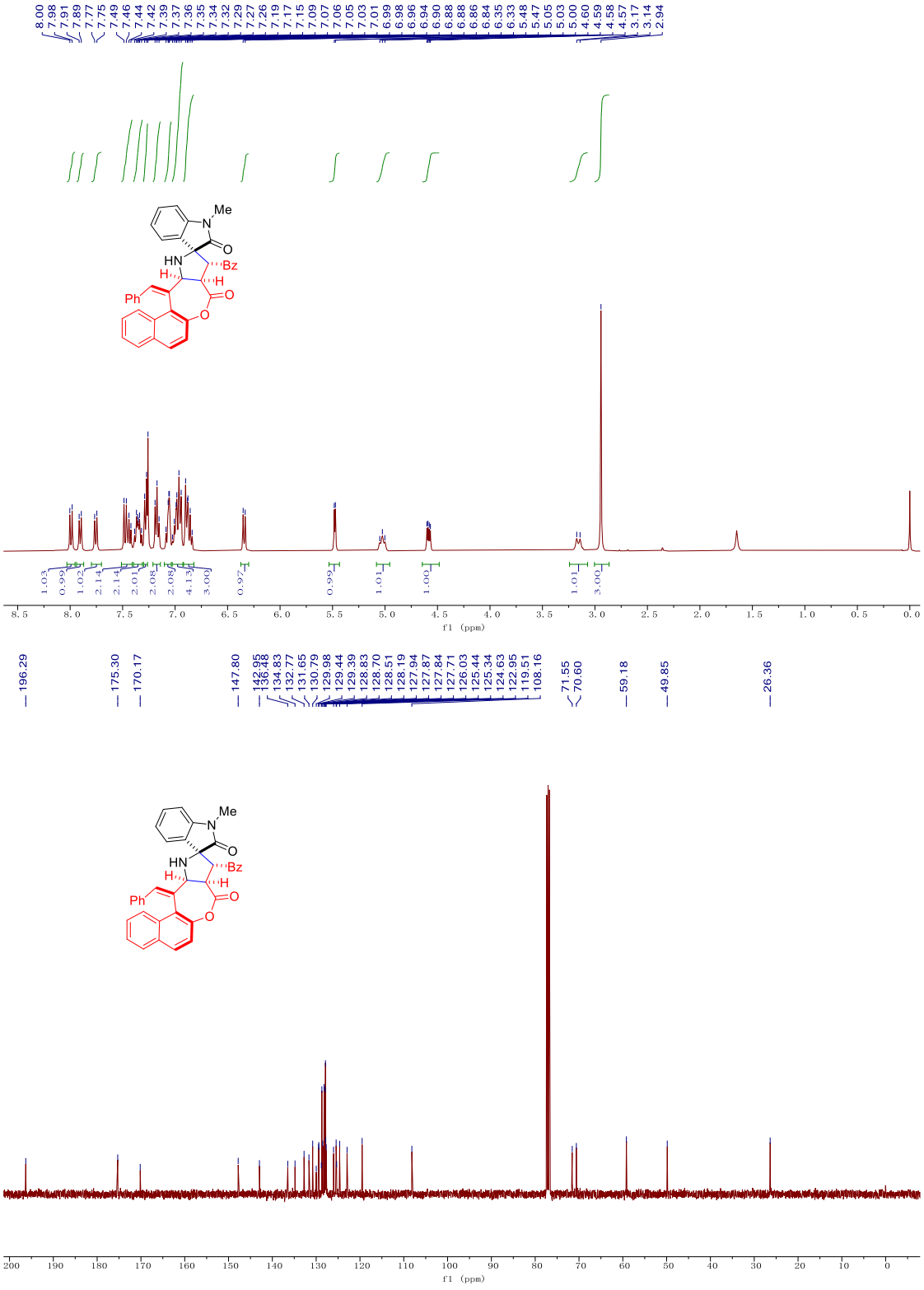
3ia


8.38
8.38
7.94
7.92
7.84
7.77
7.75
7.62
7.54
7.53
7.46
7.44
7.41
7.40
7.33
7.31
7.30
7.27
7.18
7.17
7.16
7.15
7.10
7.08
7.07
7.06
6.97
6.96
5.60
5.59
5.51
5.50
4.56
4.55
4.54
2.80
1.56
Ph
N
N
Ph
O
HN
H
Bz
H
Ph
O
Br
O
2.04
1.04
1.00
1.10
3.07
3.10
4.02
2.01
4.10
3.09
2.00
1.07
1.01
1.00
1.01
f1 (ppm)
195.56
173.08
170.54
155.59
148.13
137.02
136.26
134.81
133.60
131.39
131.25
130.55
130.05
130.03
129.83
129.61
129.44
129.18
128.87
128.64
128.60
128.39
128.31
128.20
128.00
127.30
126.80
125.55
124.61
122.34
119.63
118.95
72.09
65.37
55.93
47.23
f1 (ppm)

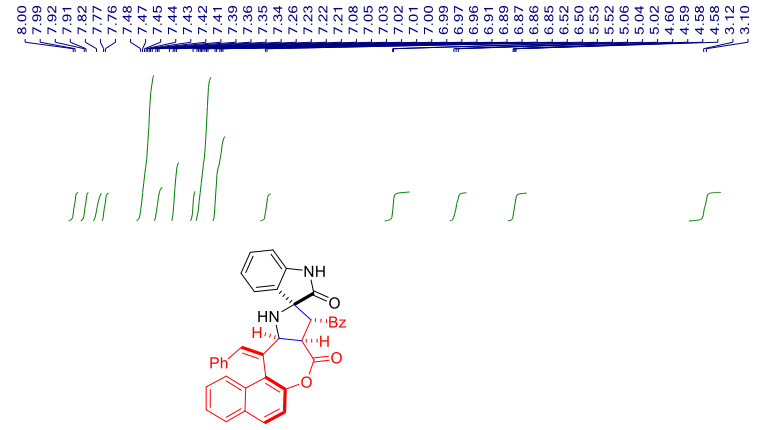
3ja


8.39
8.38
7.87
7.85
7.77
7.75
7.60
7.55
7.53
7.43
7.41
7.38
7.32
7.30
7.29
7.26
7.19
7.17
7.15
7.10
7.08
7.05
7.03
6.99
6.90
5.61
5.59
5.52
5.51
4.56
4.54
4.53
4.52
3.60
2.81
2.80
1.56
Ph
N
N
Ph
O
HN
H
Bz
H
Ph
O
MeO
O
2.01
1.02
1.08
3.02
1.99
3.09
3.04
3.02
7.10
0.99
1.02
0.99
1.00
3.12
0.99
f1 (ppm)
195.67
173.23
170.92
159.04
155.69
148.02
137.09
136.29
135.24
133.54
131.41
131.20
130.81
130.24
129.93
129.44
129.15
128.62
128.53
128.28
128.18
127.95
127.80
127.33
127.03
125.47
123.97
118.87
118.75
116.57
103.05
72.13
65.48
56.07
55.18
47.20
f1 (ppm)

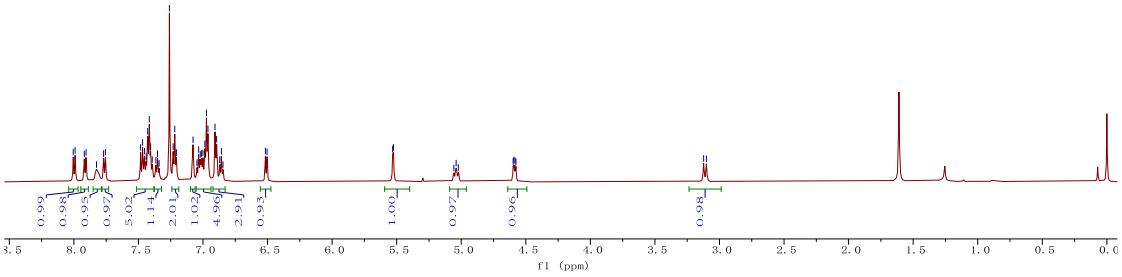
5aa

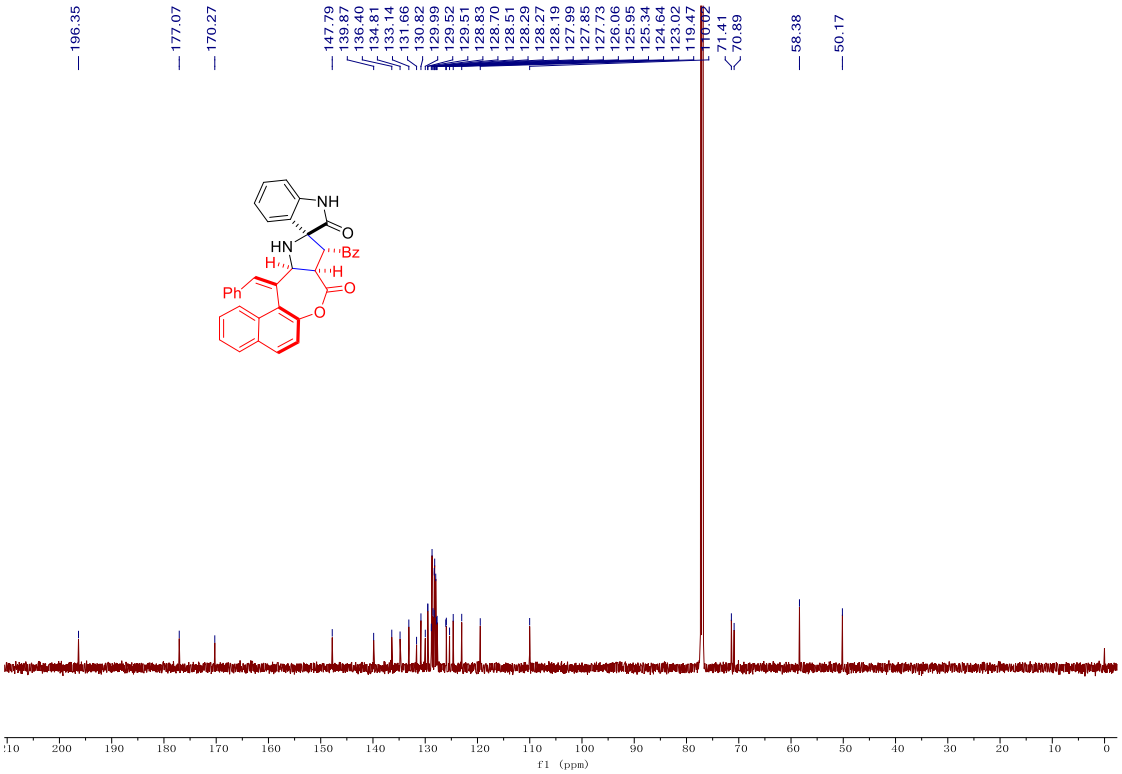

8.00 7.98 7.91 7.89 7.77 7.75 7.49 7.46 7.44 7.42 7.39 7.37 7.36 7.35 7.34 7.32 7.29 7.27 7.26 7.19 7.17 7.15 7.09 7.07 7.06 7.05 7.03 7.01 6.99 6.98 6.96 6.94 6.90 6.88 6.88 6.86 6.84 6.35 6.33 5.48 5.47 5.05 5.03 5.00 4.60 4.59 4.58 4.57 3.17 3.14 2.94
Me
N
O
HN
H
Bz
H
Ph
O
O
1.03 0.99 1.02 2.14 2.14 2.01 2.08 2.08 4.13 3.00 0.97 0.99 1.01 1.00 1.01 3.00
f1 (ppm)
196.29 175.30 170.17 147.80 142.95 136.48 134.83 132.77 131.65 130.79 129.98 129.44 129.39 128.83 128.70 128.51 128.19 127.94 127.87 127.84 127.71 126.03 125.44 125.34 124.63 122.95 119.51 108.16 71.55 70.60 59.18 49.85 26.36
f1 (ppm)

5ab


8.00
7.99
7.92
7.91
7.82
7.77
7.76
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.39
7.36
7.35
7.34
7.26
7.23
7.22
7.21
7.08
7.05
7.03
7.02
7.01
7.00
6.99
6.97
6.96
6.91
6.89
6.87
6.86
6.85
6.52
6.50
5.53
5.52
5.06
5.04
5.02
4.60
4.59
4.58
4.58
3.12
3.10

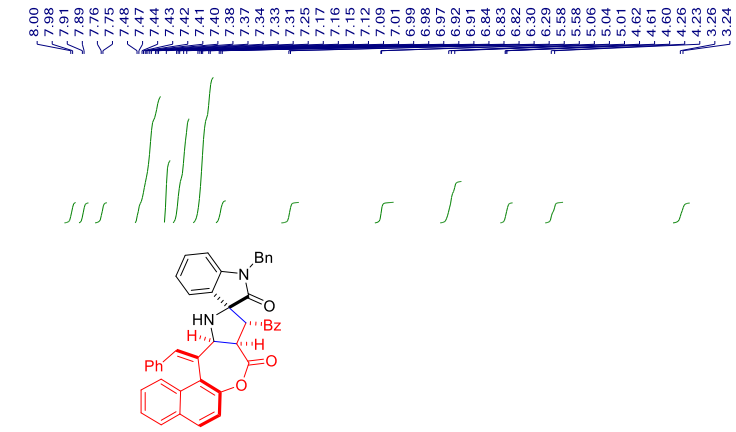
NH
O
HN
H
Bz
H
Ph
O
O


0.99
0.98
0.95
0.97
5.03
1.14
2.01
1.02
4.96
2.91
0.93
1.00
0.97
0.96
0.98
f1 (ppm)

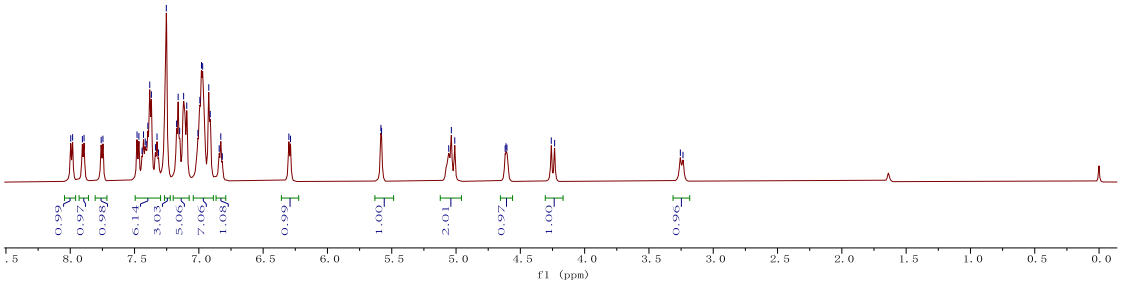

196.35
177.07
170.27
147.79
139.87
136.40
134.81
133.14
131.66
130.82
129.99
129.52
129.51
128.83
128.70
128.51
128.29
128.27
128.19
127.99
127.85
127.73
126.06
125.95
125.34
124.64
123.02
119.47
71.41
70.89
58.38
50.17
f1 (ppm)

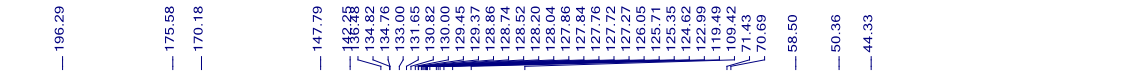
NH
O
HN
H
Bz
H
Ph
O
O

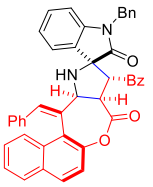
5ac


8.00
7.98
7.91
7.89
7.76
7.75
7.48
7.47
7.44
7.43
7.42
7.41
7.40
7.38
7.37
7.34
7.33
7.31
7.25
7.17
7.16
7.15
7.12
7.09
7.01
6.99
6.98
6.97
6.92
6.91
6.84
6.83
6.82
6.30
6.29
5.58
5.58
5.06
5.04
5.01
4.62
4.61
4.60
4.26
4.23
3.26
3.24

Bn
N
O
HN
H
Bz
H
Ph
O
O

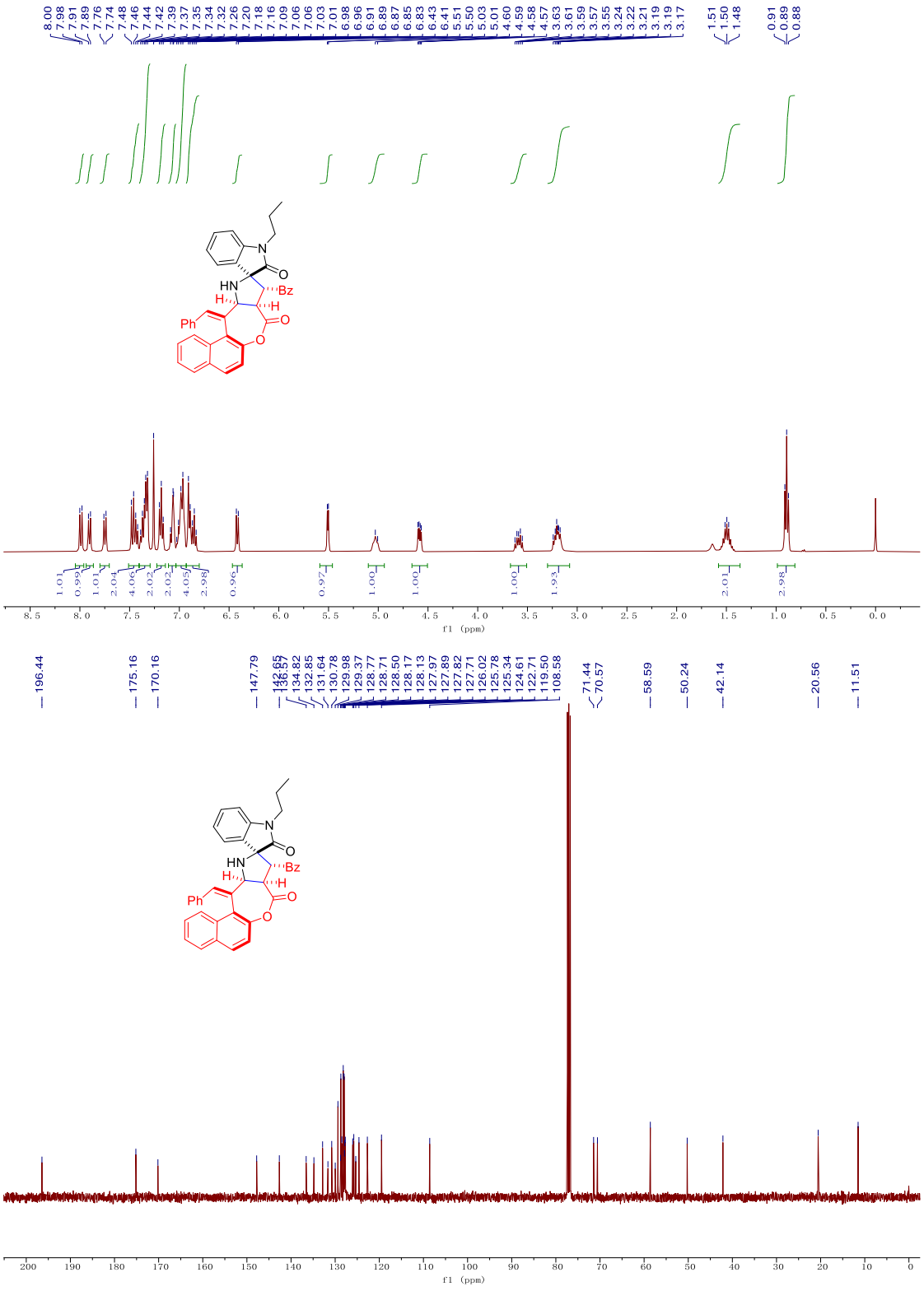

0.93
0.97
0.98
6.14
3.03
5.06
7.06
1.08
0.99
1.00
2.01
0.97
1.00
0.96
f1 (ppm)


196.29
175.58
170.18
147.79
142.35
136.48
134.82
134.76
133.00
131.65
130.82
130.00
129.45
129.37
128.86
128.74
128.52
128.20
128.04
127.86
127.84
127.76
127.72
127.27
126.05
125.71
125.35
124.62
122.99
119.49
109.42
71.43
70.69
58.50
50.36
44.33

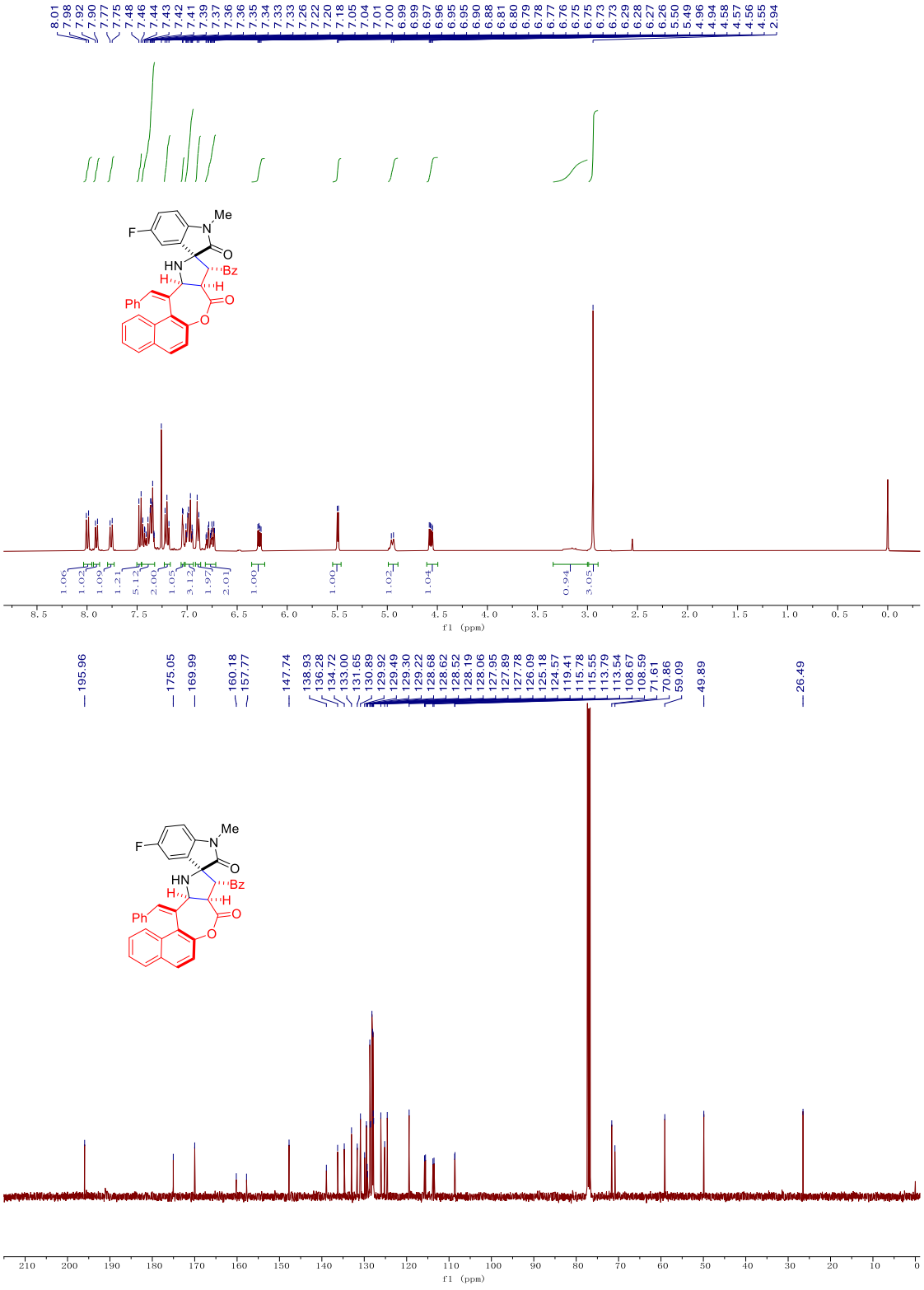

Bn
N
O
HN
H
Bz
H
Ph
O
O

f1 (ppm)

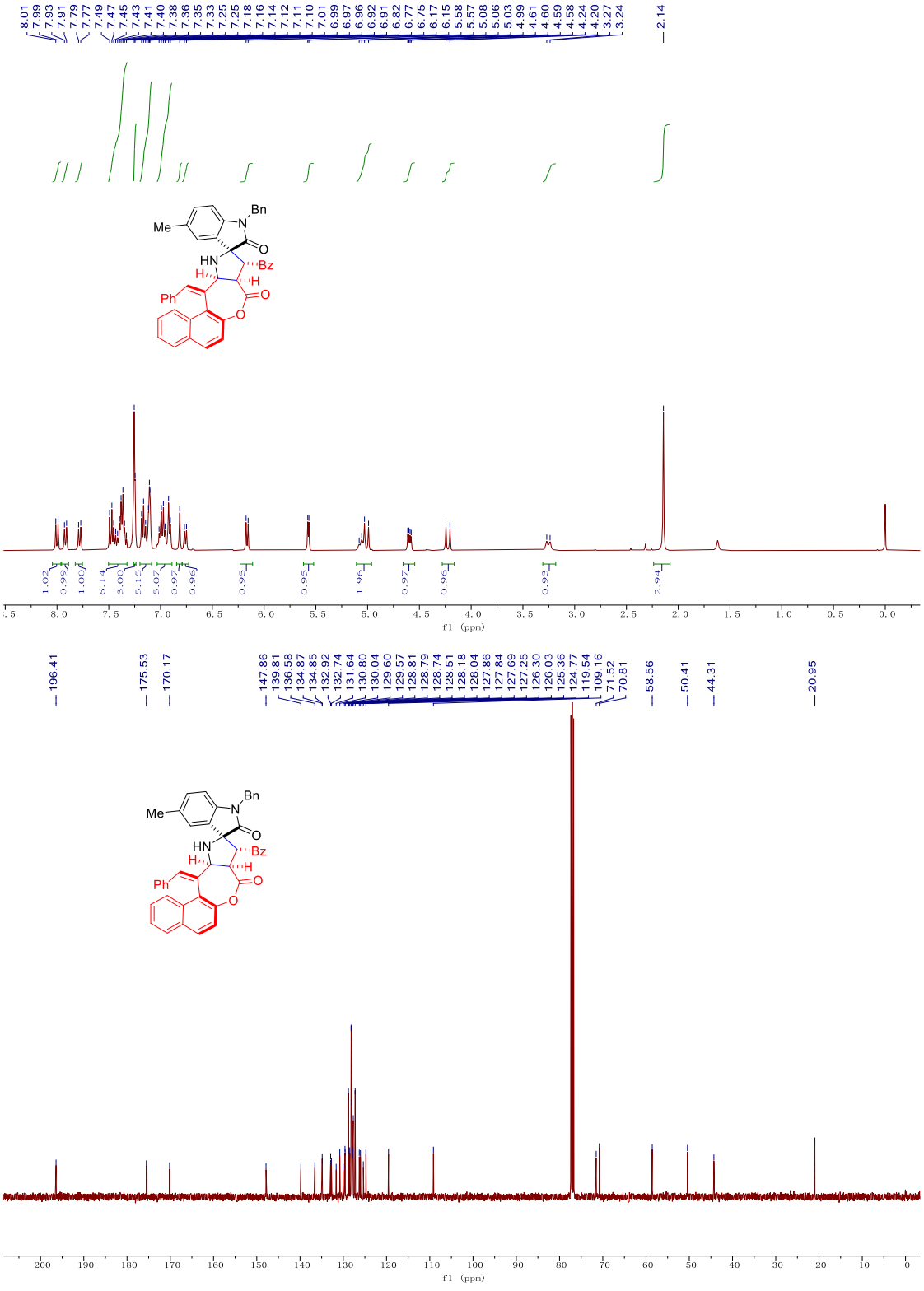
5ad


8.00 7.98 7.91 7.89 7.76 7.74 7.48 7.46 7.44 7.42 7.39 7.37 7.35 7.34 7.32 7.26 7.20 7.18 7.16 7.09 7.06 7.06 7.03 7.01 6.98 6.96 6.91 6.89 6.87 6.85 6.83 6.43 6.41 5.51 5.50 5.03 5.01 4.60 4.59 4.58 4.57 3.63 3.61 3.59 3.57 3.55 3.24 3.22 3.21 3.19 3.19 3.17 1.51 1.50 1.48 0.91 0.89 0.88
N
O
HN
H
Bz
H
Ph
O
O
1.01 0.99 1.01 2.04 4.06 2.02 2.02 4.05 2.98 0.96 0.97 1.00 1.00 1.00 1.93 2.01 2.98
f1 (ppm)
196.44 175.16 170.16 147.79 142.65 138.57 134.82 132.85 131.64 130.78 129.98 129.37 128.77 128.71 128.50 128.17 128.13 127.97 127.89 127.82 127.71 126.02 125.78 125.34 124.61 122.71 119.50 108.58 71.44 70.57 58.59 50.24 42.14 20.56 11.51
f1 (ppm)

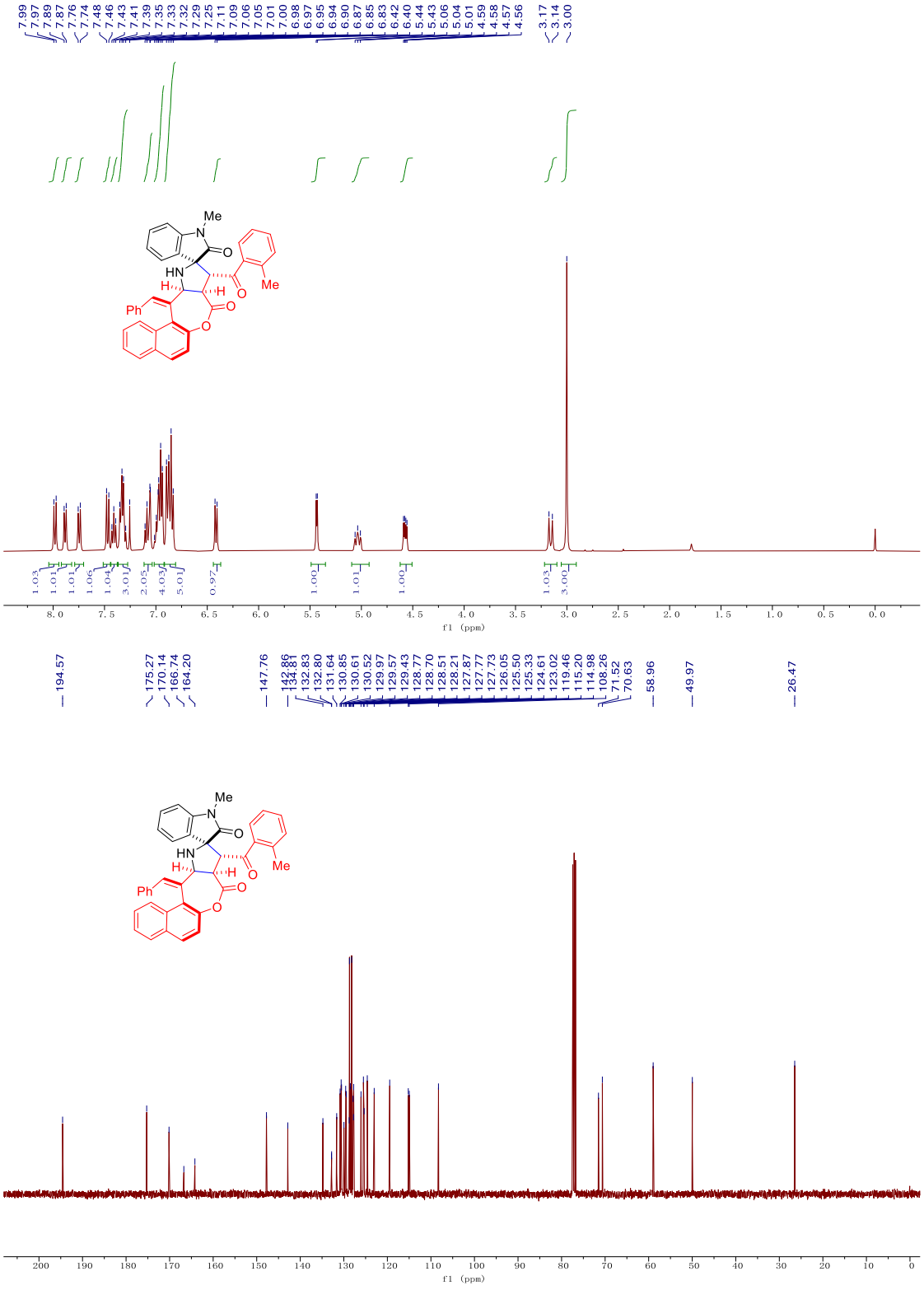
5ae


8.01 7.98 7.92 7.90 7.77 7.75 7.48 7.46 7.44 7.43 7.42 7.41 7.39 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.26 7.22 7.20 7.18 7.05 7.04 7.01 7.00 6.99 6.99 6.97 6.96 6.95 6.95 6.90 6.88 6.81 6.80 6.79 6.78 6.77 6.76 6.75 6.75 6.73 6.73 6.29 6.28 6.27 6.26 5.50 5.49 4.96 4.94 4.58 4.57 4.56 4.55 2.94
F
Me
N
O
HN
H
Bz
H
Ph
O
O
1.06 1.02 1.09 1.21 5.12 2.00 1.05 3.12 1.97 2.01 1.00 1.00 1.02 1.04 0.94 3.05
f1 (ppm)
195.96 175.05 169.99 160.18 157.77 147.74 138.93 136.28 134.72 133.00 131.65 130.89 129.92 129.49 129.30 129.22 128.88 128.62 128.52 128.19 128.06 127.95 127.89 127.78 126.09 125.18 124.57 119.41 115.78 115.55 113.79 113.54 108.67 108.59 71.61 70.86 59.09 49.89 26.49
f1 (ppm)

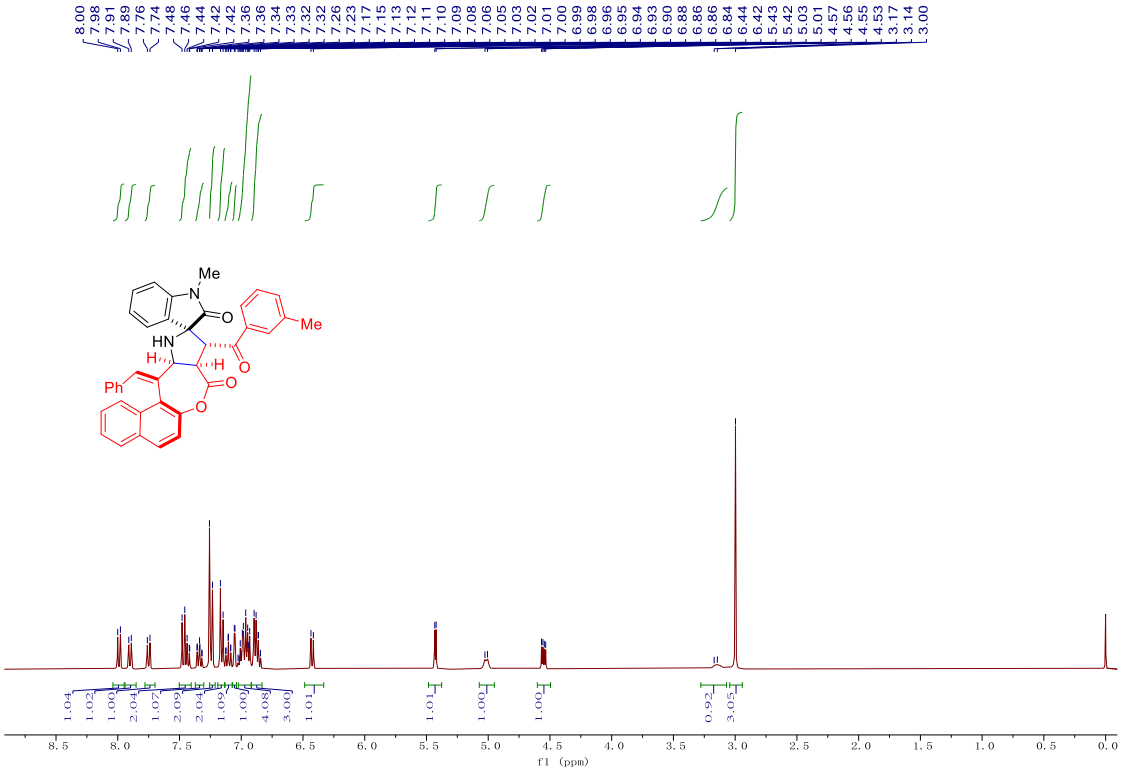
5af

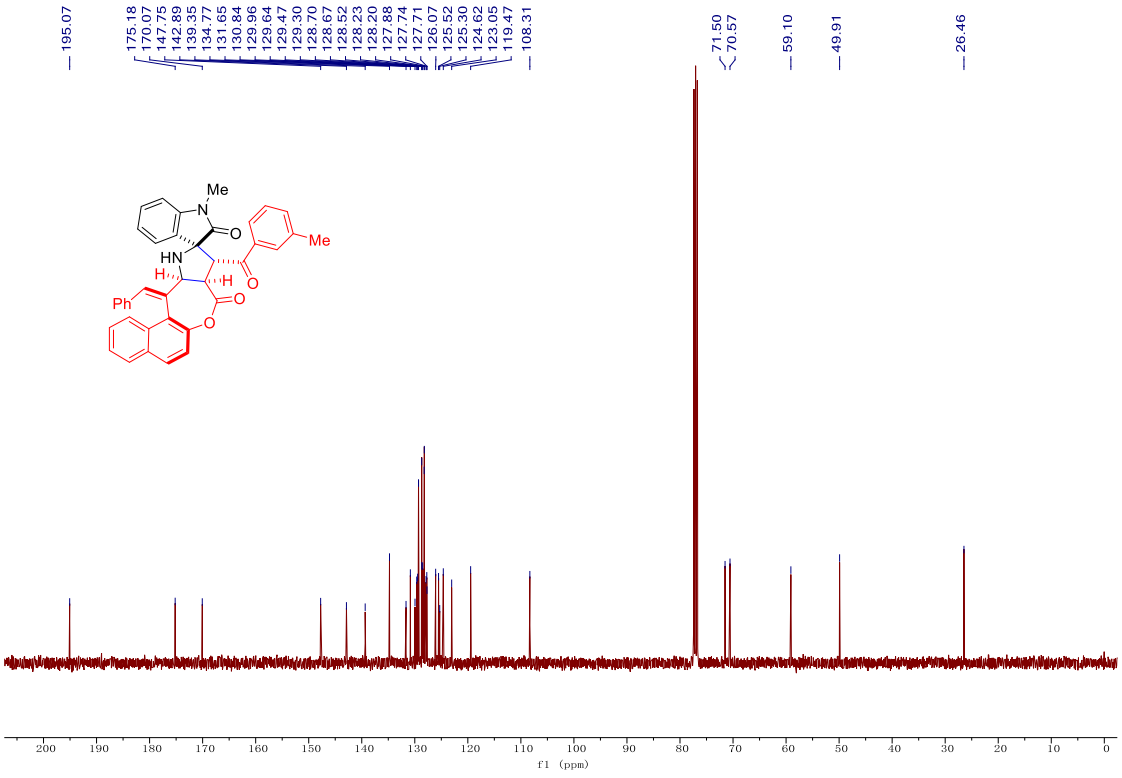

8.01 7.99 7.93 7.91 7.79 7.77 7.49 7.47 7.45 7.43 7.41 7.40 7.38 7.36 7.35 7.33 7.25 7.18 7.16 7.14 7.12 7.11 7.10 7.01 6.99 6.97 6.96 6.92 6.91 6.82 6.77 6.75 6.17 6.15 5.58 5.57 5.08 5.06 5.03 4.99 4.61 4.60 4.59 4.58 4.24 4.20 3.27 3.24 2.14
Me
N
Bn
O
HN
H
Bz
H
O
Ph
O
1.02 0.99 1.00 6.14 3.00 5.15 5.07 0.97 0.96 0.93 0.95 1.96 0.97 0.96 0.93 2.94
f1 (ppm)
196.41 175.53 170.17 147.86 139.81 136.58 134.87 134.85 132.92 132.74 131.64 130.80 130.04 129.60 129.57 128.81 128.79 128.74 128.51 128.18 128.04 127.86 127.84 127.69 127.25 126.30 126.03 125.36 124.77 119.54 109.16 71.52 70.81 58.56 50.41 44.31 20.95
Me
N
Bn
O
HN
H
Bz
H
O
Ph
O
f1 (ppm)

5ba

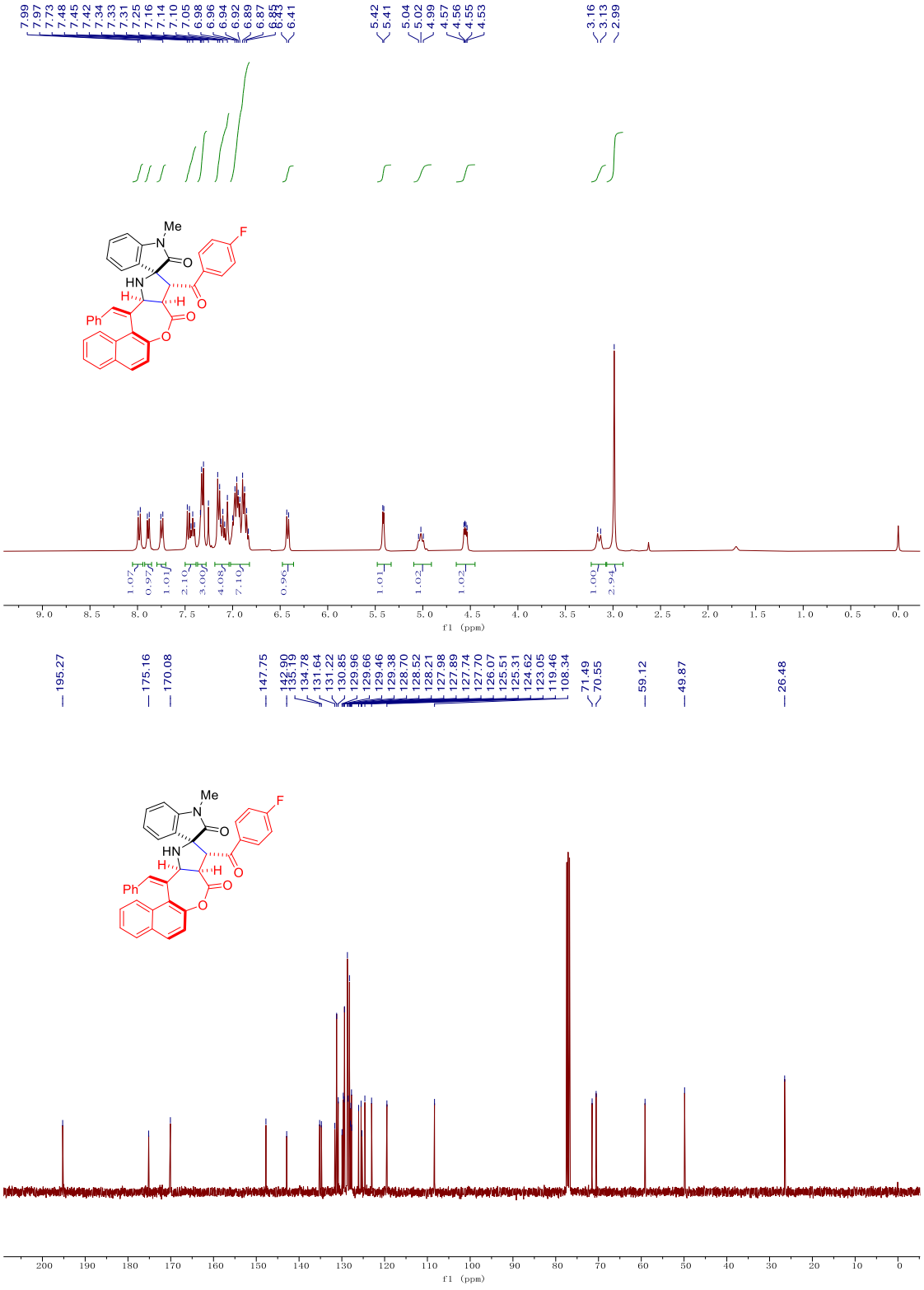

7.99
7.97
7.89
7.87
7.76
7.74
7.48
7.46
7.43
7.41
7.39
7.35
7.33
7.32
7.29
7.25
7.11
7.09
7.06
7.05
7.01
7.00
6.98
6.97
6.95
6.94
6.90
6.87
6.85
6.83
6.42
6.40
5.44
5.43
5.06
5.04
5.01
4.59
4.58
4.57
4.56
3.17
3.14
3.00
Me
N
O
HN
H
H
O
Me
Ph
O
O
1.03
1.01
1.01
1.06
1.04
3.01
2.05
4.03
5.01
0.97
1.00
1.01
1.00
1.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
194.57
175.27
170.14
166.74
164.20
147.76
142.86
134.81
132.83
132.80
131.64
130.85
130.61
130.52
129.97
129.57
129.43
128.77
128.70
128.51
128.21
127.87
127.77
127.73
126.05
125.50
125.33
124.61
123.02
119.46
115.20
114.98
108.26
71.52
70.63
58.96
49.97
26.47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5ca

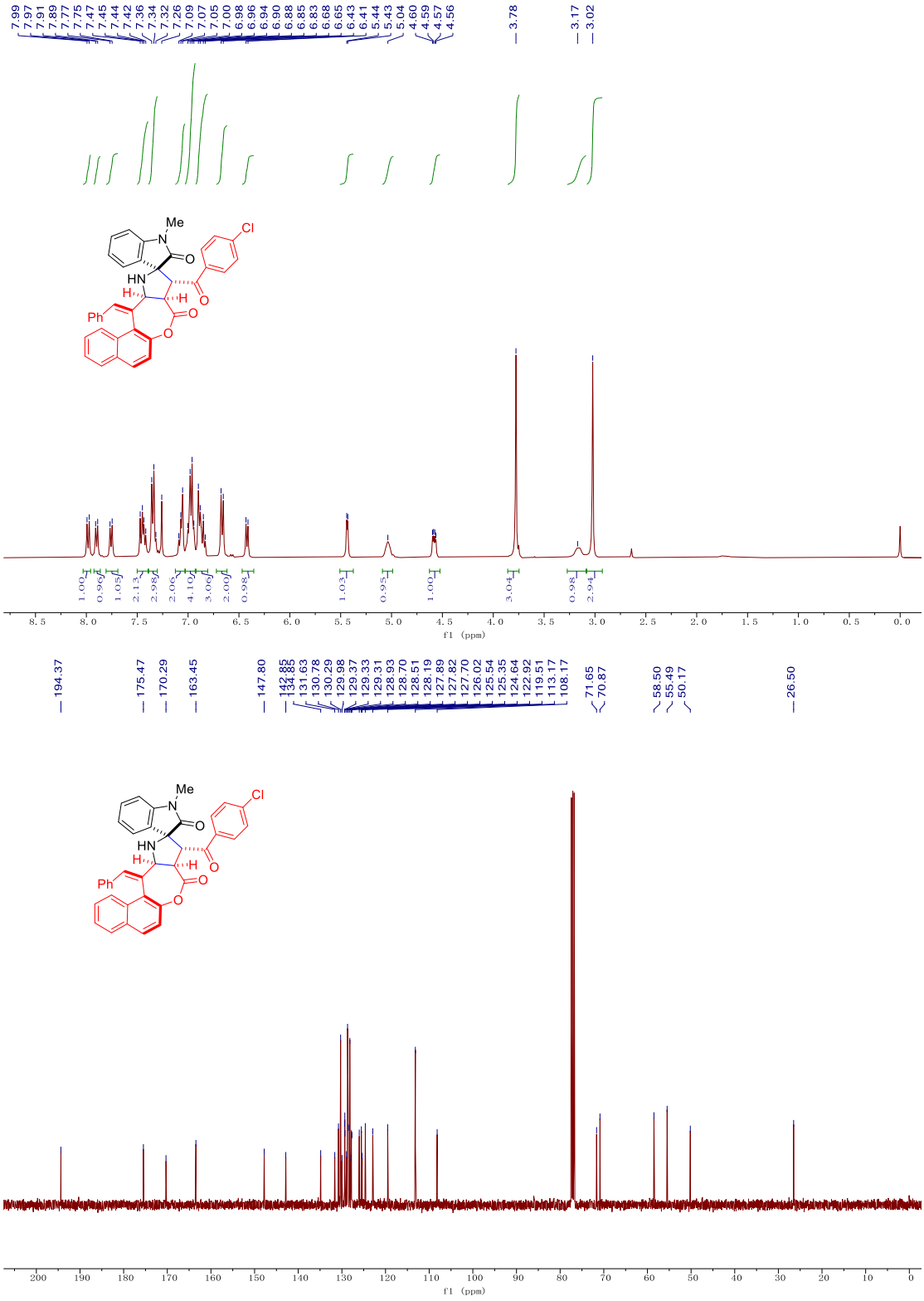

8.00 7.98 7.91 7.89 7.76 7.74 7.48 7.46 7.44 7.42 7.42 7.36 7.36 7.34 7.33 7.32 7.32 7.26 7.23 7.17 7.15 7.13 7.12 7.11 7.10 7.09 7.08 7.06 7.05 7.03 7.02 7.01 7.00 6.99 6.98 6.96 6.95 6.94 6.93 6.90 6.88 6.86 6.86 6.84 6.44 6.42 5.43 5.42 5.03 5.01 4.57 4.56 4.55 4.53 3.17 3.14 3.00
Me
N
O
HN
H
H
O
Me
Ph
O
O
1.04 1.02 1.00 2.04 1.07 2.09 2.04 1.09 1.00 4.08 3.00 1.01 1.01 1.00 1.00 0.92 3.05
f1 (ppm)


195.07
175.18 170.07 147.75 142.89 139.35 134.77 131.65 130.84 129.96 129.64 129.47 129.30 128.70 128.67 128.52 128.23 128.20 127.88 127.74 127.71 126.07 125.52 125.30 124.62 123.05 119.47
108.31
71.50 70.57
59.10
49.91
26.46
Me
N
O
HN
H
H
O
Me
Ph
O
O
f1 (ppm)

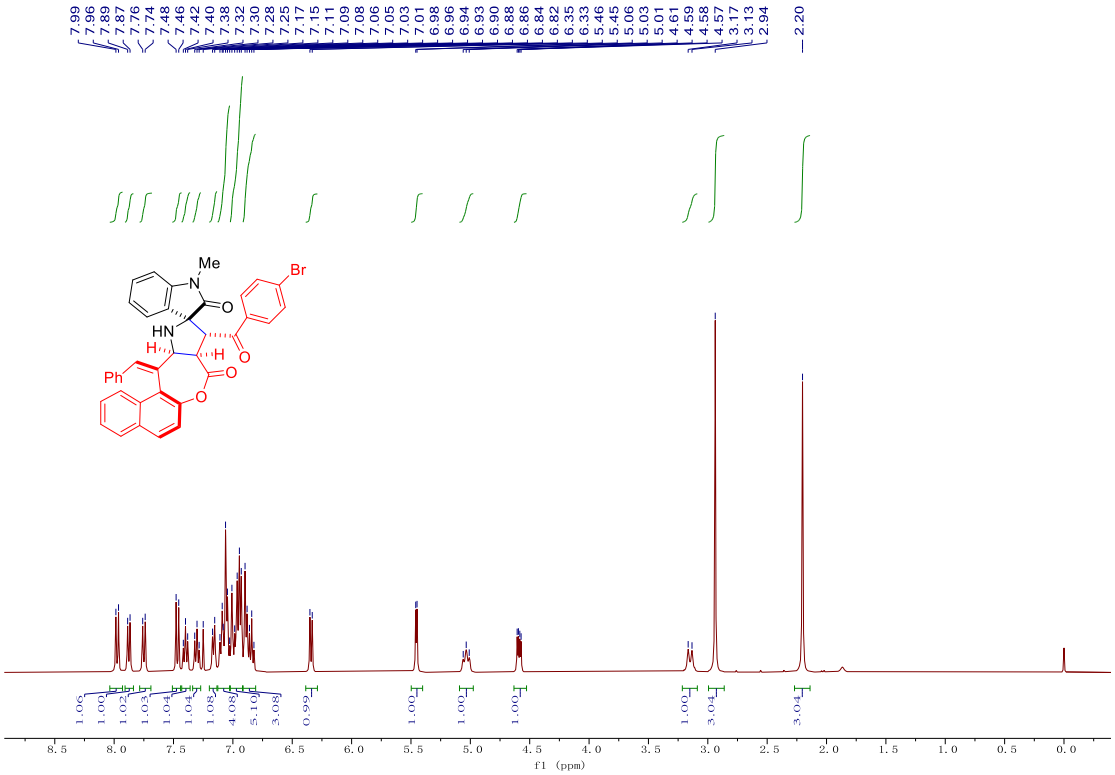
5da

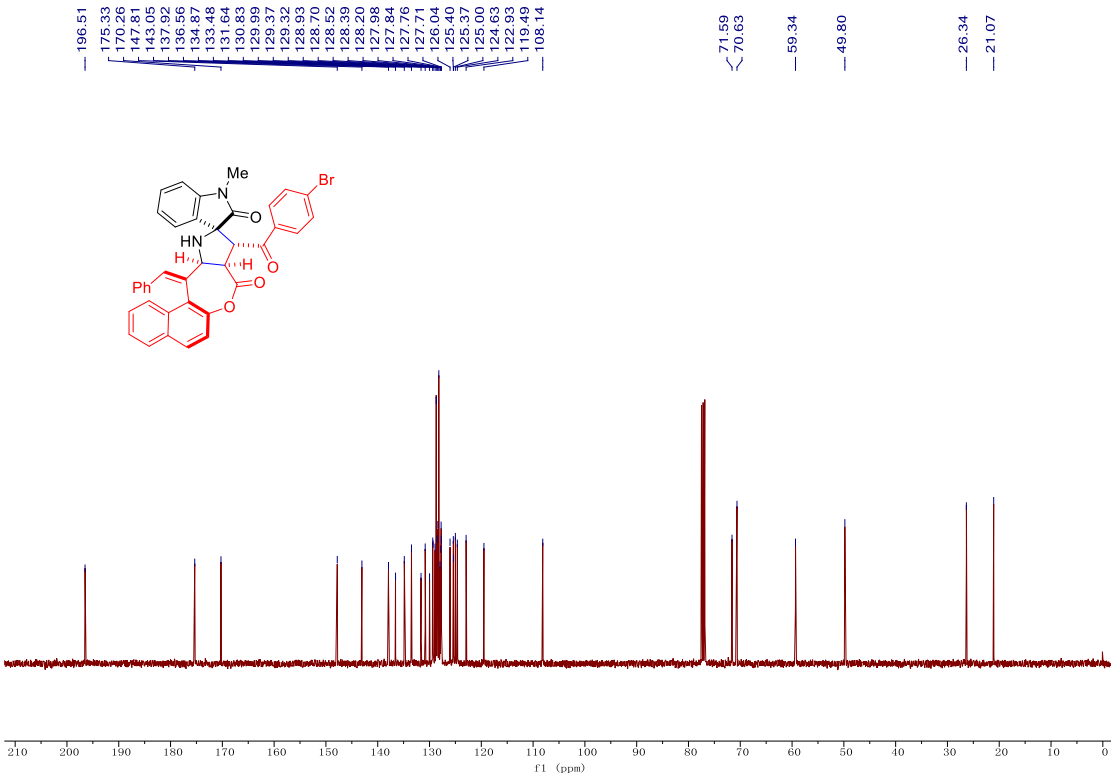

7.99
7.97
7.73
7.48
7.45
7.42
7.34
7.33
7.31
7.25
7.16
7.14
7.10
7.05
6.98
6.96
6.94
6.92
6.89
6.87
6.43
6.41
5.42
5.41
5.04
5.02
4.99
4.57
4.56
4.55
4.53
3.16
3.13
2.99
Me
N
O
HN
H
H
O
O
Ph
O
F
1.07
0.97
1.01
2.10
3.00
4.08
7.10
0.96
1.01
1.02
1.02
1.00
2.94
f1 (ppm)
195.27
175.16
170.08
147.75
142.90
135.19
134.78
131.64
131.22
130.85
129.96
129.66
129.46
129.38
128.70
128.52
128.21
127.98
127.89
127.74
127.70
126.07
125.51
125.31
124.62
123.05
119.46
108.34
71.49
70.55
59.12
49.87
26.48
f1 (ppm)

5ea

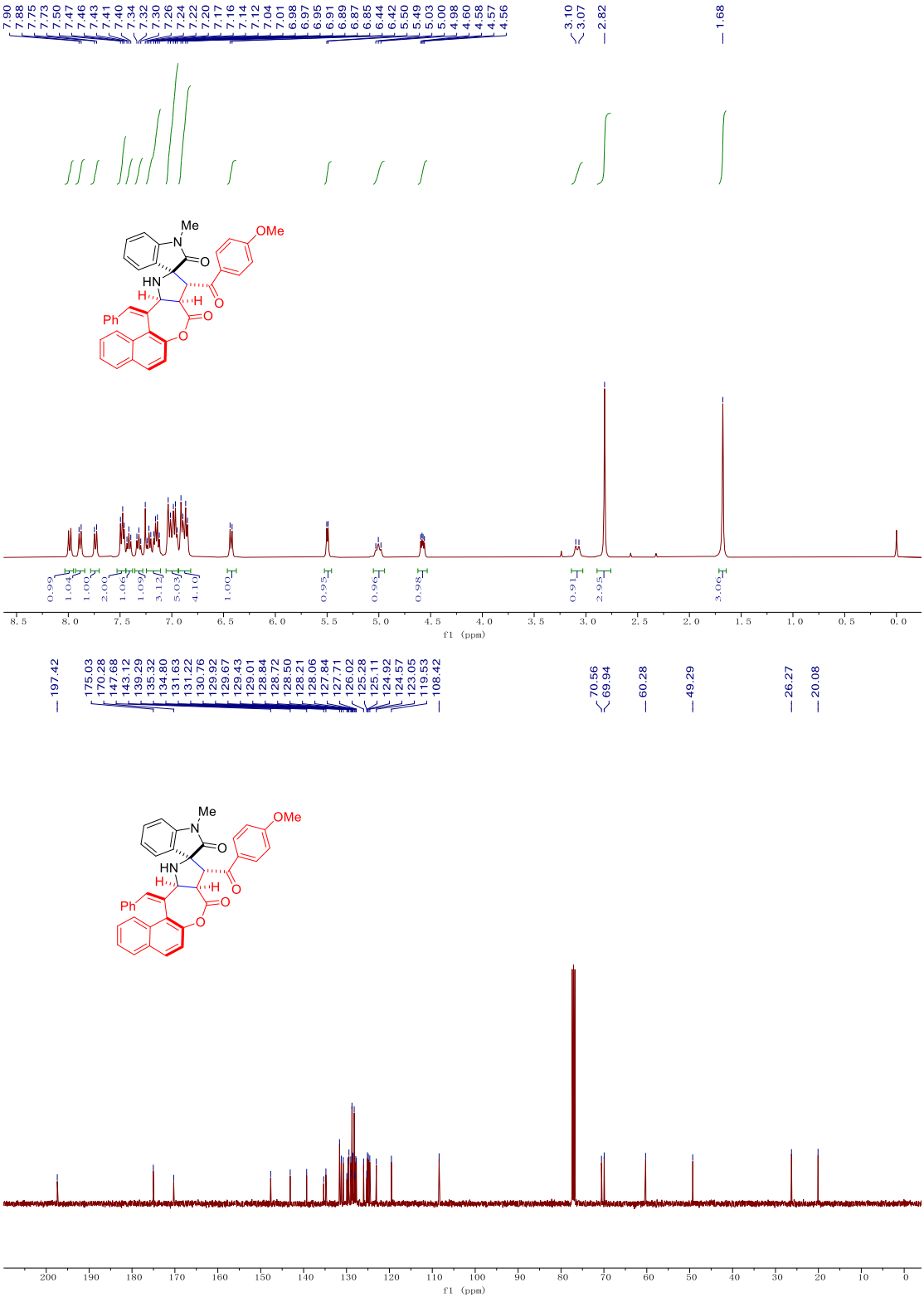

7.99
7.97
7.91
7.89
7.77
7.75
7.47
7.45
7.44
7.42
7.36
7.34
7.32
7.26
7.09
7.07
7.05
7.00
6.98
6.96
6.94
6.90
6.88
6.85
6.83
6.68
6.65
6.43
6.41
5.44
5.43
5.04
4.60
4.59
4.57
4.56
3.78
3.17
3.02
Me
N
O
HN
H
H
O
O
Ph
O
Cl
1.00
0.99
1.05
2.13
2.98
2.06
4.10
3.06
2.00
0.98
1.03
0.95
1.00
3.04
0.98
2.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
194.37
175.47
170.29
163.45
147.80
142.85
142.65
141.63
131.63
130.78
130.29
129.98
129.37
129.33
129.31
128.93
128.70
128.51
128.19
127.89
127.82
127.70
126.02
125.54
125.35
124.64
122.92
119.51
113.17
108.17
71.65
70.87
58.50
55.49
50.17
26.50
Me
N
O
HN
H
H
O
O
Ph
O
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5fa

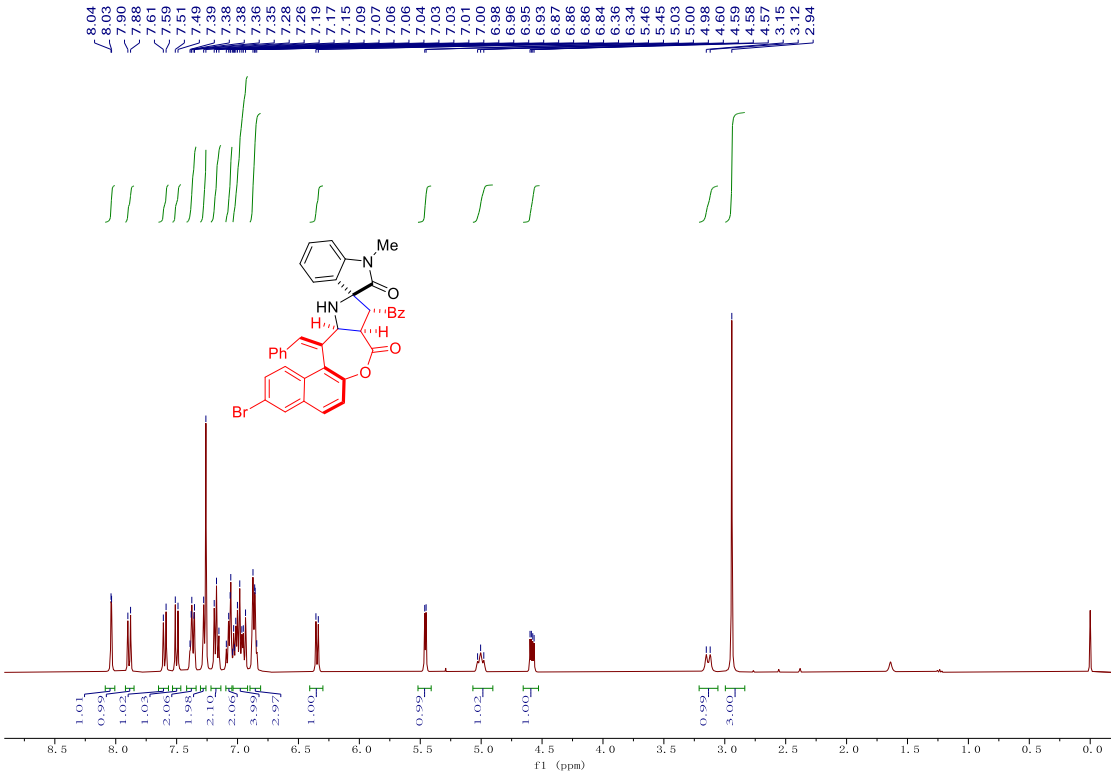

7.99 7.96 7.89 7.87 7.76 7.74 7.48 7.46 7.42 7.40 7.38 7.32 7.30 7.28 7.25 7.17 7.15 7.11 7.09 7.08 7.06 7.05 7.03 7.01 6.98 6.96 6.94 6.93 6.90 6.88 6.86 6.84 6.82 6.35 6.33 5.46 5.45 5.06 5.03 5.01 4.61 4.59 4.58 4.57 3.17 3.13 2.94 2.20
Me
N
O
HN
H
H
O
Br
O
Ph
O
1.06 1.00 1.02 1.03 1.04 1.04 1.08 4.08 5.10 3.08 0.99 1.00 1.00 1.00 1.00 3.04 3.04
f1 (ppm)

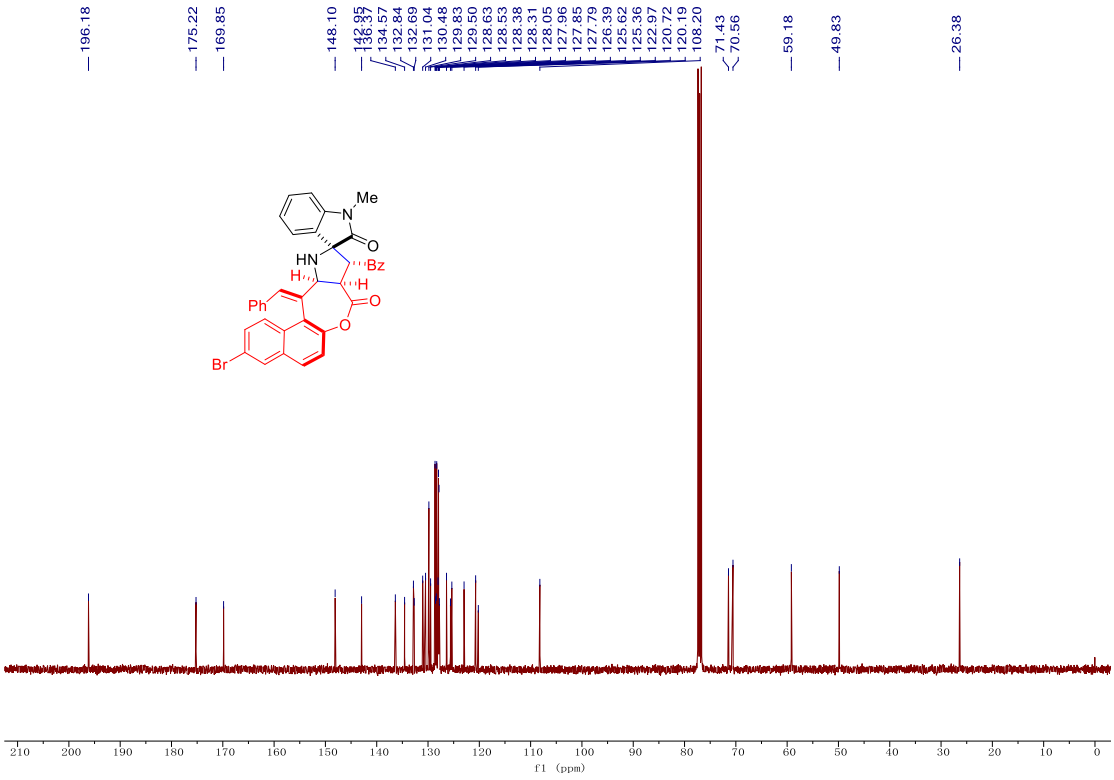

196.51 175.33 170.26 147.81 143.05 137.92 136.56 134.87 133.48 131.64 130.83 129.99 129.37 129.32 128.93 128.70 128.52 128.39 128.20 127.98 127.84 127.76 127.71 126.04 125.40 125.37 125.00 124.63 122.93 119.49 108.14 71.59 70.63 59.34 49.80 26.34 21.07
Me
N
O
HN
H
H
O
Br
O
Ph
O
f1 (ppm)

5ga

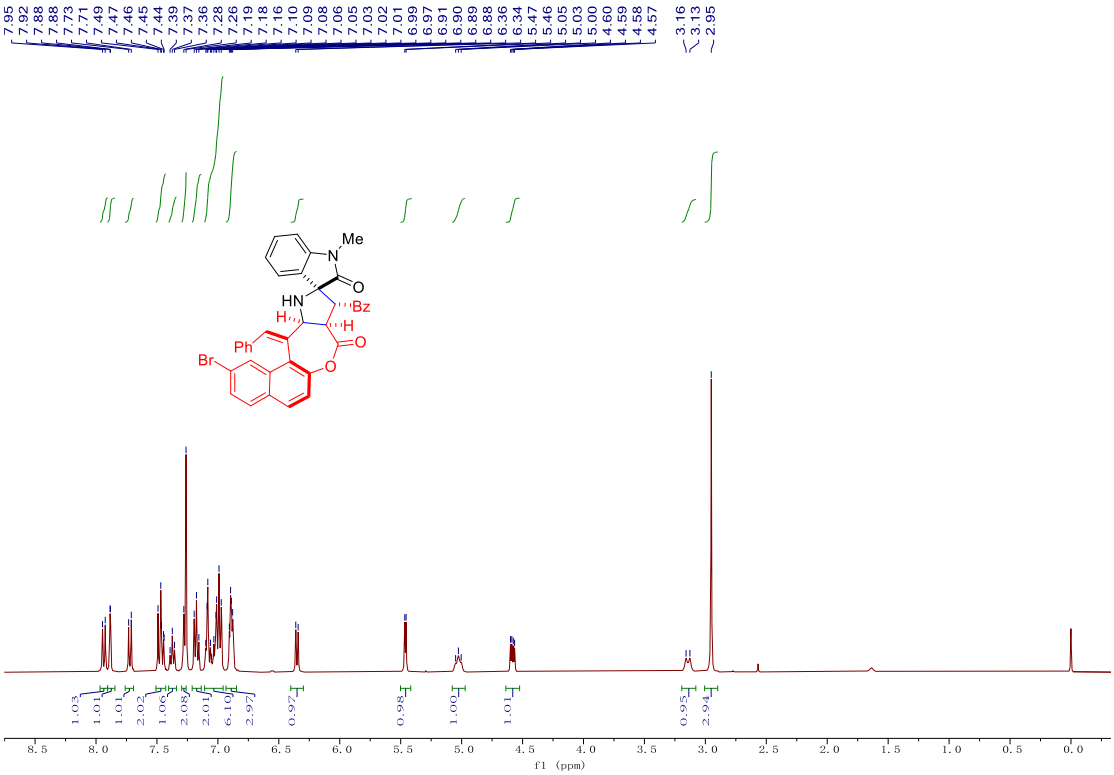

7.90 7.88 7.75 7.73 7.50 7.47 7.46 7.43 7.41 7.40 7.34 7.32 7.30 7.26 7.24 7.22 7.20 7.17 7.16 7.14 7.12 7.04 7.01 6.98 6.97 6.95 6.91 6.89 6.87 6.85 6.44 6.42 5.50 5.49 5.03 5.00 4.98 4.60 4.58 4.57 4.56
3.10 3.07 2.82 1.68
Me
N
O
OMe
HN
H
H
O
O
Ph
O
0.93 1.04 1.00 2.00 1.06 1.09 3.12 5.03 4.10 1.00 0.95 0.96 0.98 0.91 2.95 3.06
f1 (ppm)
197.42
175.03 170.28 147.68 143.12 139.29 135.32 134.80 131.63 131.22 130.76 129.92 129.67 129.43 129.01 128.84 128.72 128.50 128.21 128.06 127.84 127.71 126.02 125.28 125.11 124.92 124.57 123.05 119.53 108.42
70.56 69.94 60.28 49.29 26.27 20.08
f1 (ppm)

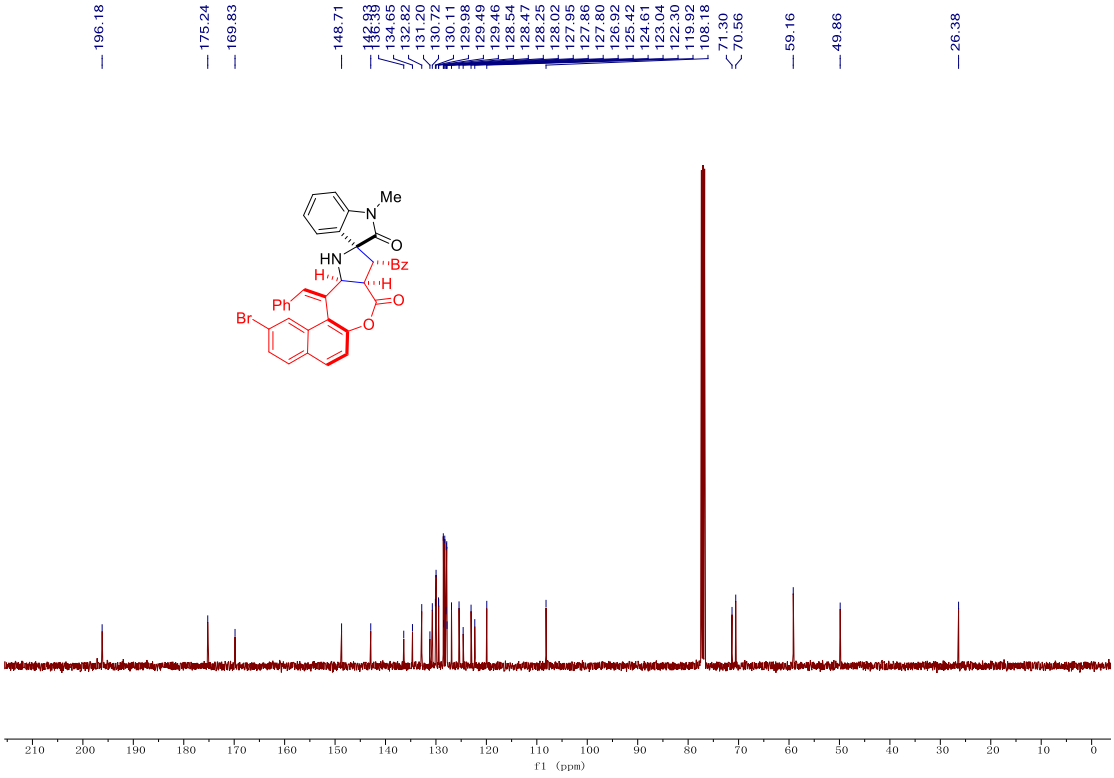
5ha


8.04
8.03
7.90
7.88
7.61
7.59
7.51
7.49
7.39
7.38
7.38
7.36
7.35
7.28
7.26
7.19
7.17
7.15
7.09
7.07
7.06
7.06
7.04
7.03
7.03
7.01
7.00
6.98
6.96
6.95
6.93
6.87
6.86
6.86
6.84
6.36
6.34
5.46
5.45
5.03
5.00
4.98
4.60
4.59
4.58
4.57
3.15
3.12
2.94
Me
N
O
HN
H
Bz
H
Ph
O
O
Br
1.01
0.99
1.02
1.03
2.06
1.98
2.10
2.06
3.99
2.97
1.00
0.99
1.02
1.00
0.99
3.00
f1 (ppm)

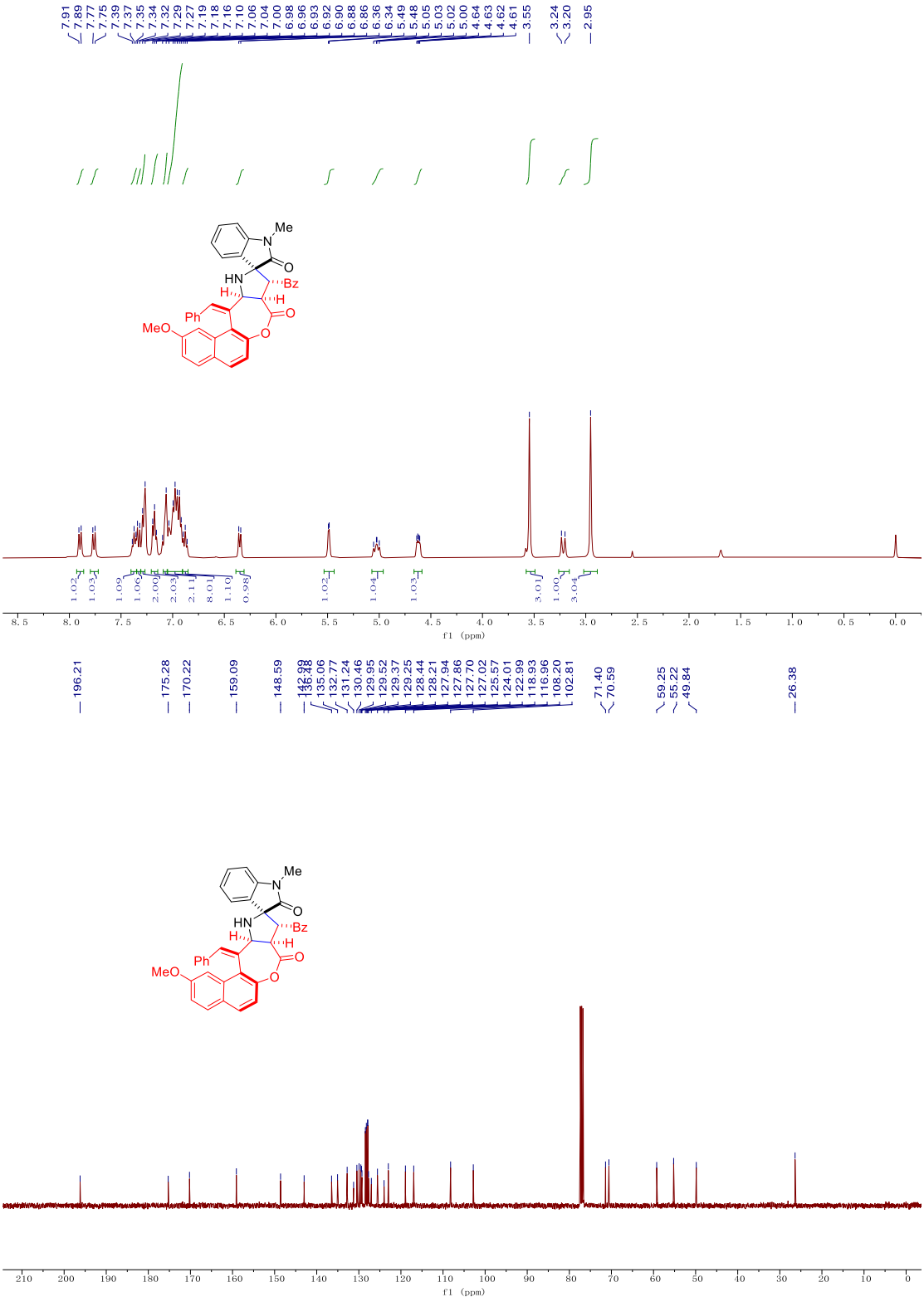

196.18
175.22
169.85
148.10
142.85
138.37
134.57
132.84
132.69
131.04
130.48
129.83
129.50
128.63
128.53
128.38
128.31
128.05
127.96
127.85
127.79
126.39
125.62
125.36
122.97
120.72
120.19
108.20
71.43
70.56
59.18
49.83
26.38
Me
N
O
HN
H
Bz
H
Ph
O
O
Br
f1 (ppm)

5ia

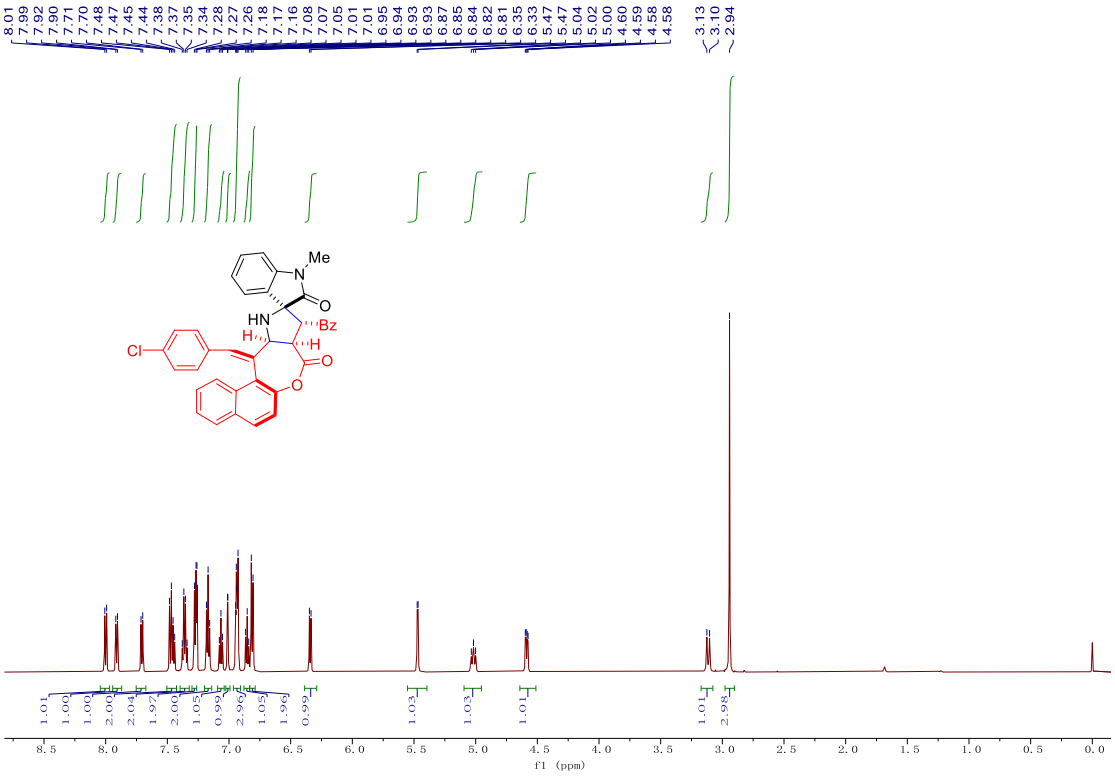

7.95 7.92 7.88 7.88 7.73 7.71 7.49 7.47 7.46 7.45 7.44 7.39 7.37 7.36 7.28 7.26 7.19 7.18 7.16 7.10 7.09 7.08 7.06 7.05 7.03 7.02 7.01 6.99 6.97 6.91 6.90 6.89 6.88 6.36 6.34 5.47 5.46 5.05 5.03 5.00 4.60 4.59 4.58 4.57 3.16 3.13 2.95
Me
N
O
HN
H
Bz
H
Ph
O
Br
O
1.03 1.01 1.01 2.02 1.06 2.08 2.01 6.10 2.97 0.97 0.98 1.00 1.01 0.95 2.94
f1 (ppm)

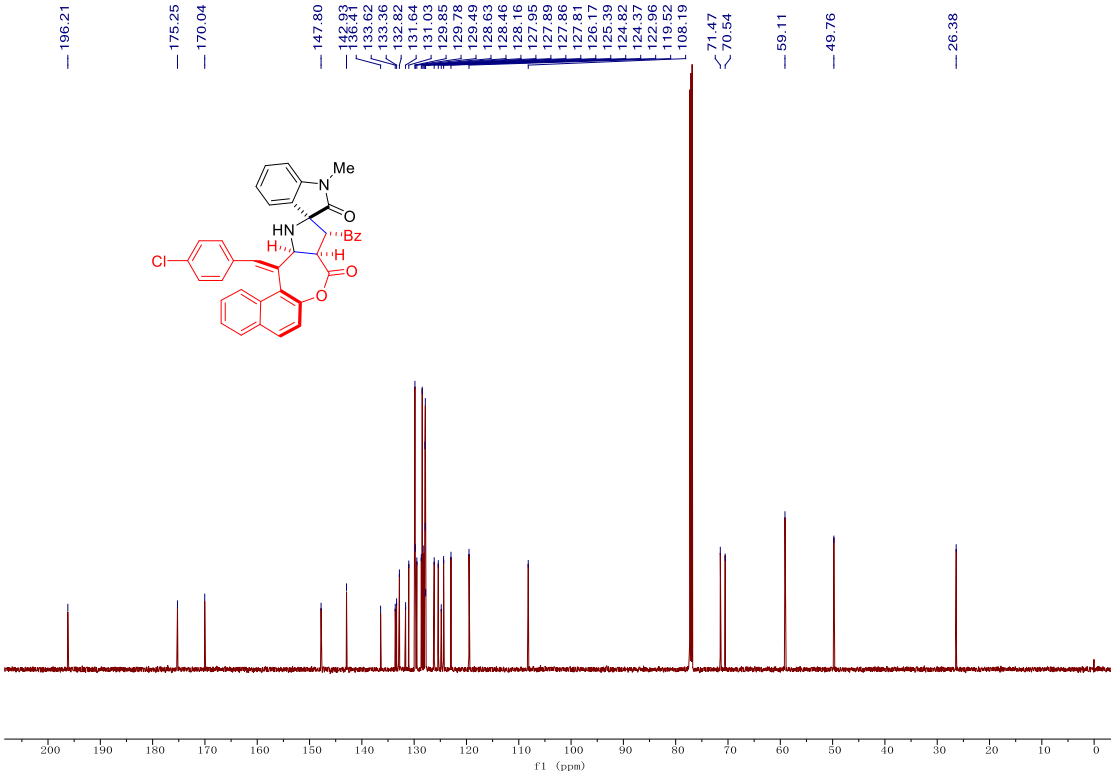

196.18 175.24 169.83 148.71 142.93 136.33 134.65 132.82 131.20 130.72 130.11 129.98 129.49 129.46 128.54 128.47 128.25 128.02 127.95 127.86 127.80 126.92 125.42 124.61 123.04 122.30 119.92 108.18 71.30 70.56 59.16 49.86 26.38
Me
N
O
HN
H
Bz
H
Ph
O
Br
O
f1 (ppm)

5ja

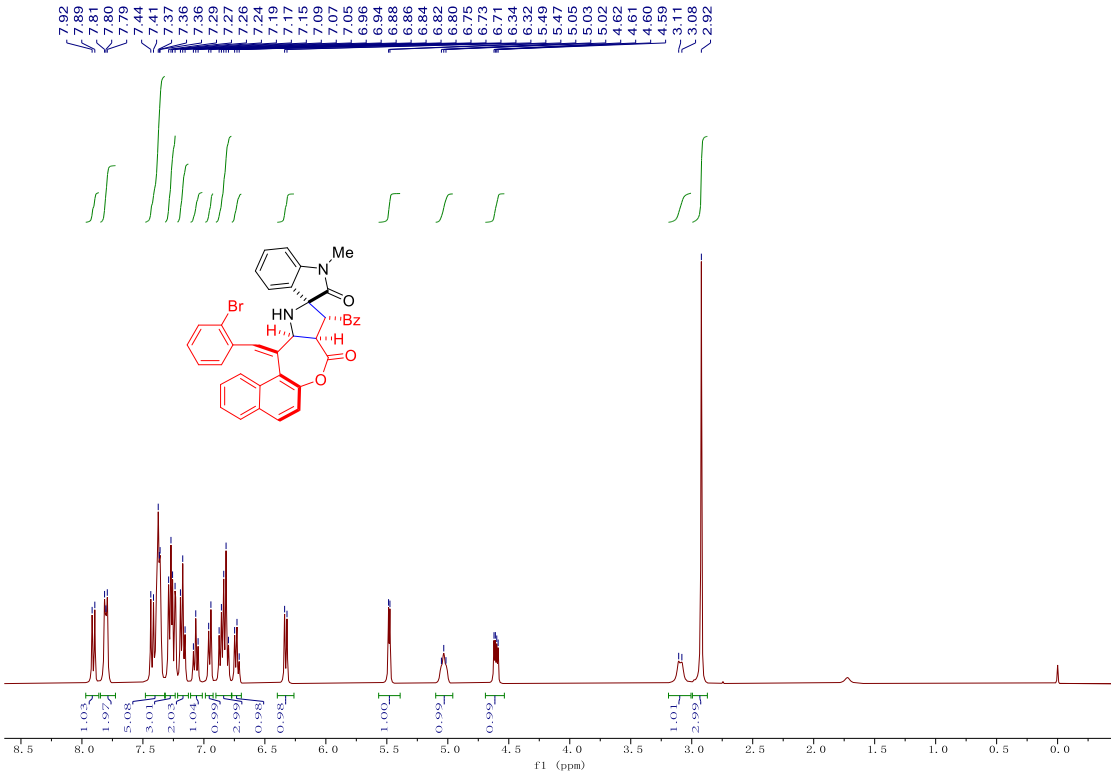

7.91
7.89
7.77
7.75
7.39
7.37
7.35
7.34
7.32
7.29
7.27
7.19
7.18
7.16
7.10
7.06
7.04
7.00
6.98
6.96
6.93
6.92
6.90
6.88
6.86
6.36
6.34
5.49
5.48
5.05
5.03
5.02
5.00
4.64
4.63
4.62
4.61
3.55
3.24
3.20
2.95
Me
N
O
HN
H
Bz
H
O
Ph
MeO
O
1.02
1.03
1.09
1.06
2.00
2.03
2.11
8.01
1.10
0.98
1.02
1.04
1.03
3.01
1.00
3.04
f1 (ppm)
196.21
175.28
170.22
159.09
148.59
142.99
136.48
135.06
132.77
131.24
130.46
129.95
129.52
129.37
129.25
128.44
128.21
127.94
127.86
127.70
127.02
125.57
124.01
122.99
118.93
116.96
108.20
102.81
71.40
70.59
59.25
55.22
49.84
26.38
f1 (ppm)

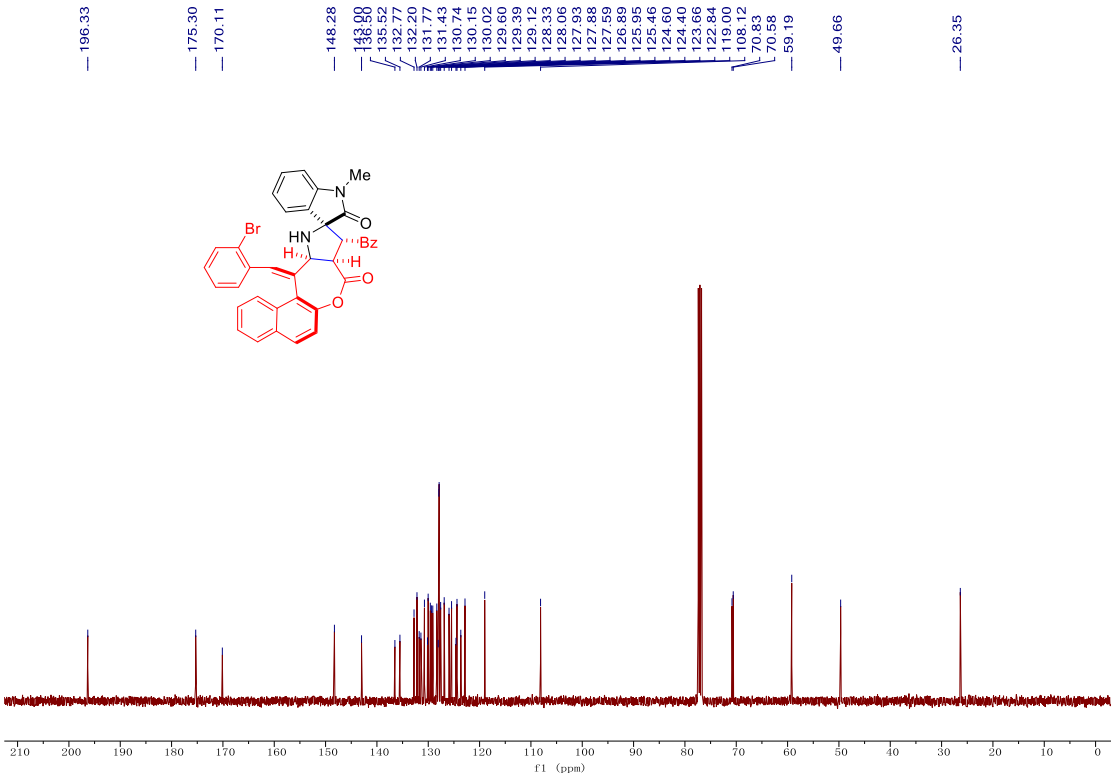
5ka


8.01
7.99
7.92
7.90
7.71
7.70
7.48
7.47
7.45
7.44
7.38
7.37
7.35
7.34
7.28
7.27
7.26
7.18
7.17
7.16
7.08
7.07
7.05
7.01
7.01
6.95
6.94
6.93
6.93
6.87
6.85
6.84
6.82
6.81
6.35
6.33
5.47
5.47
5.04
5.02
5.00
4.60
4.59
4.58
4.58
3.13
3.10
2.94
Me
N
O
HN
H
Bz
H
O
Cl
O
1.01
1.00
1.00
2.00
2.04
1.97
2.00
1.05
0.99
2.96
1.05
1.96
0.99
1.03
1.03
1.01
1.01
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

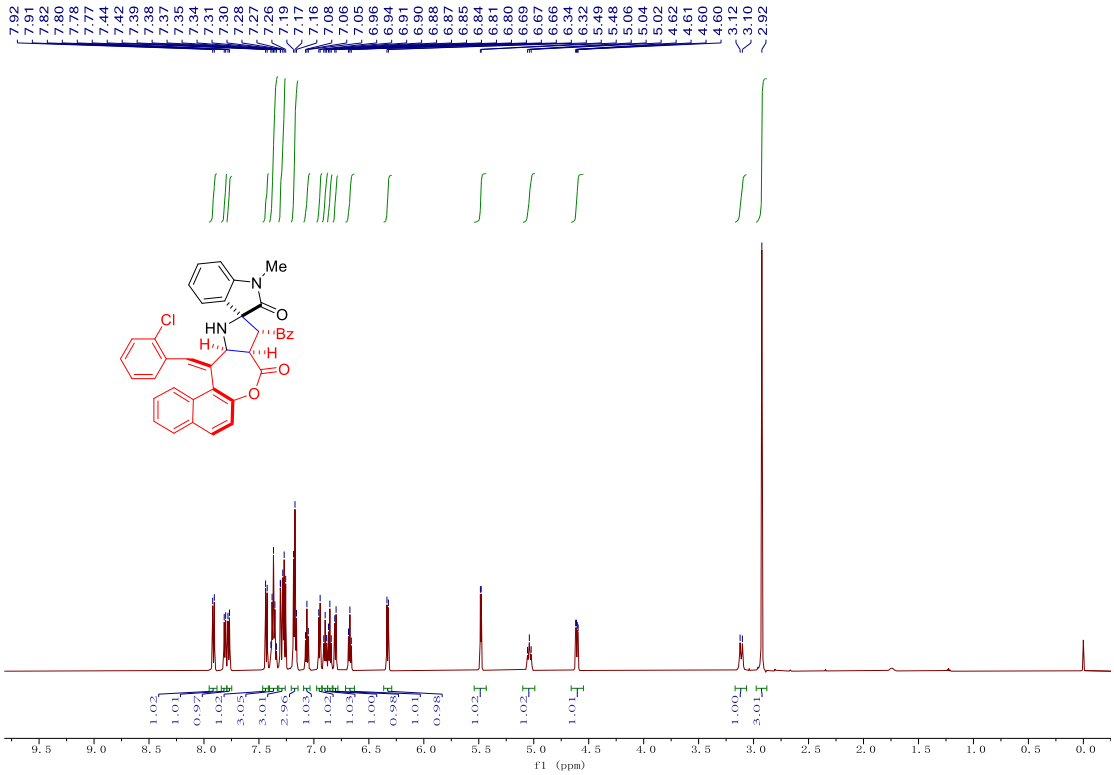

196.21
175.25
170.04
147.80
142.93
138.41
133.62
133.36
132.82
131.64
131.03
129.85
129.78
129.49
128.63
128.46
128.16
127.95
127.89
127.86
127.81
126.17
125.39
124.82
124.37
122.96
119.52
108.19
71.47
70.54
59.11
49.76
26.38
Me
N
O
HN
H
Bz
H
O
Cl
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

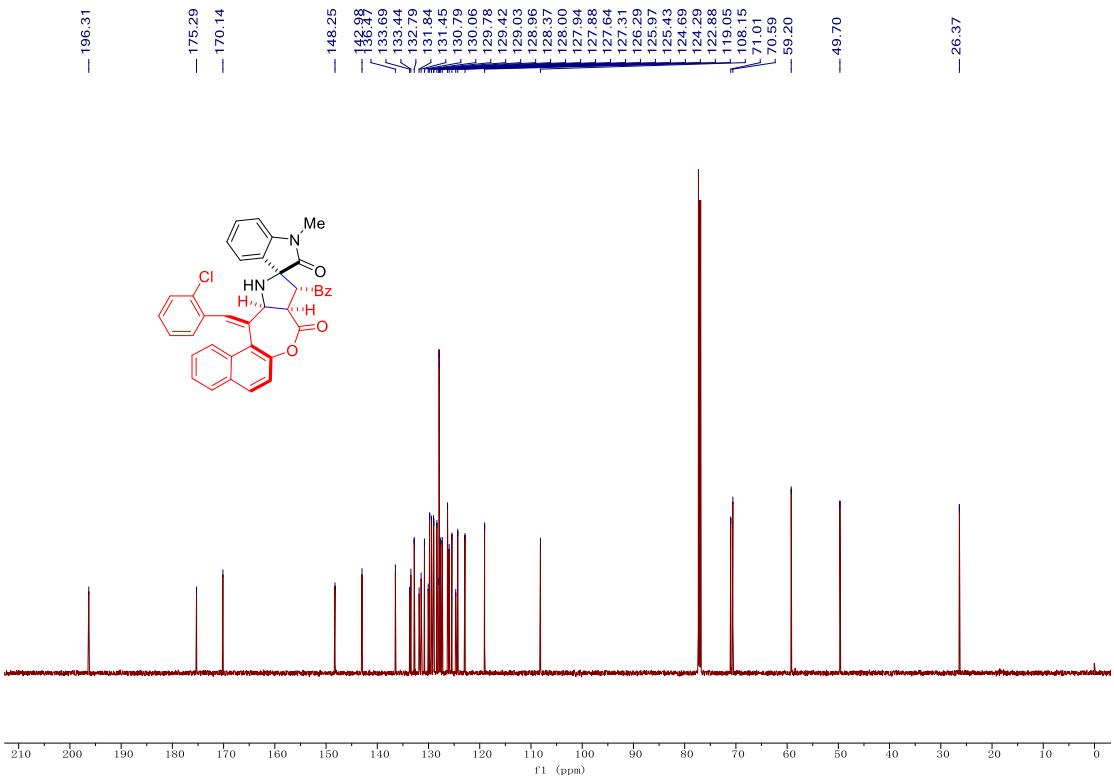
5la


7.92
7.89
7.81
7.80
7.79
7.44
7.41
7.37
7.36
7.36
7.29
7.27
7.26
7.24
7.19
7.17
7.15
7.09
7.07
7.05
6.96
6.94
6.88
6.86
6.84
6.82
6.80
6.75
6.73
6.71
6.34
6.32
5.49
5.47
5.05
5.03
5.02
4.62
4.61
4.60
4.59
3.11
3.08
2.92
Me
N
O
HN
H
Bz
H
O
Br
O
1.03
1.97
5.08
3.01
2.03
1.04
0.99
2.99
0.98
0.98
1.00
0.99
0.99
1.01
2.99
f1 (ppm)

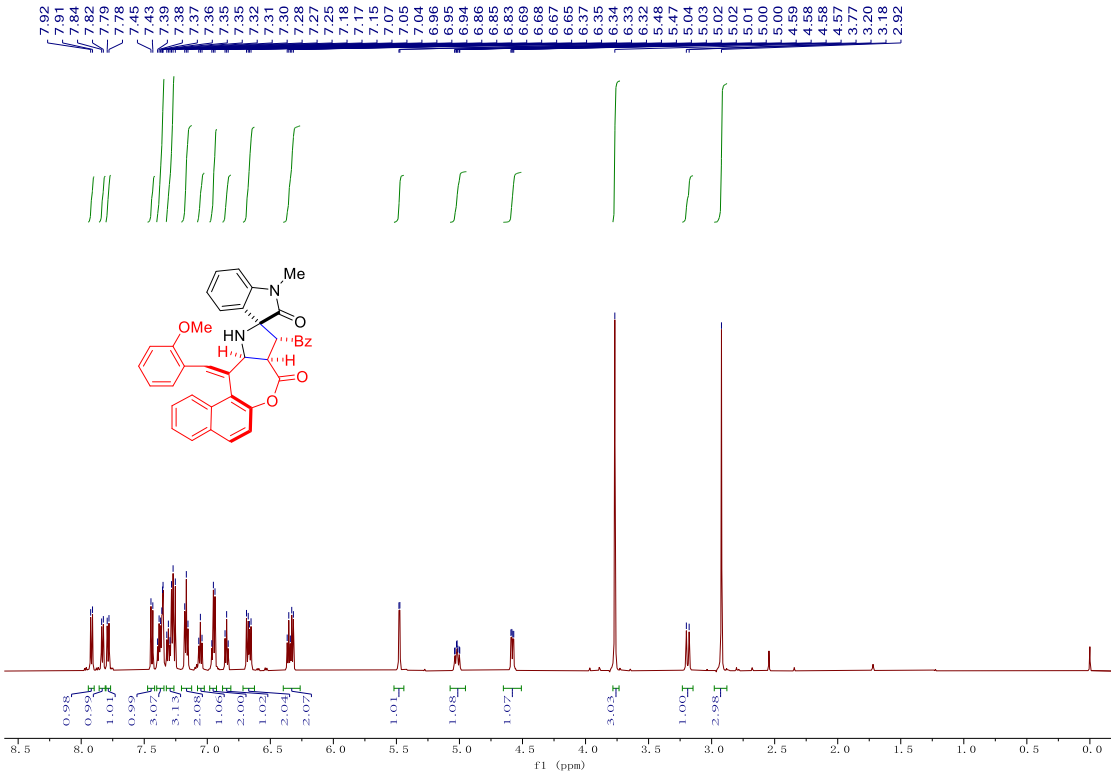

196.33
175.30
170.11
148.28
143.00
138.50
135.52
132.77
132.20
131.77
131.43
130.74
130.15
130.02
129.60
129.39
129.12
128.33
128.06
127.93
127.88
127.59
126.89
125.95
125.46
124.60
124.40
123.66
122.84
119.00
108.12
70.83
70.58
59.19
49.66
26.35
Me
N
O
HN
H
Bz
H
O
Br
O
f1 (ppm)

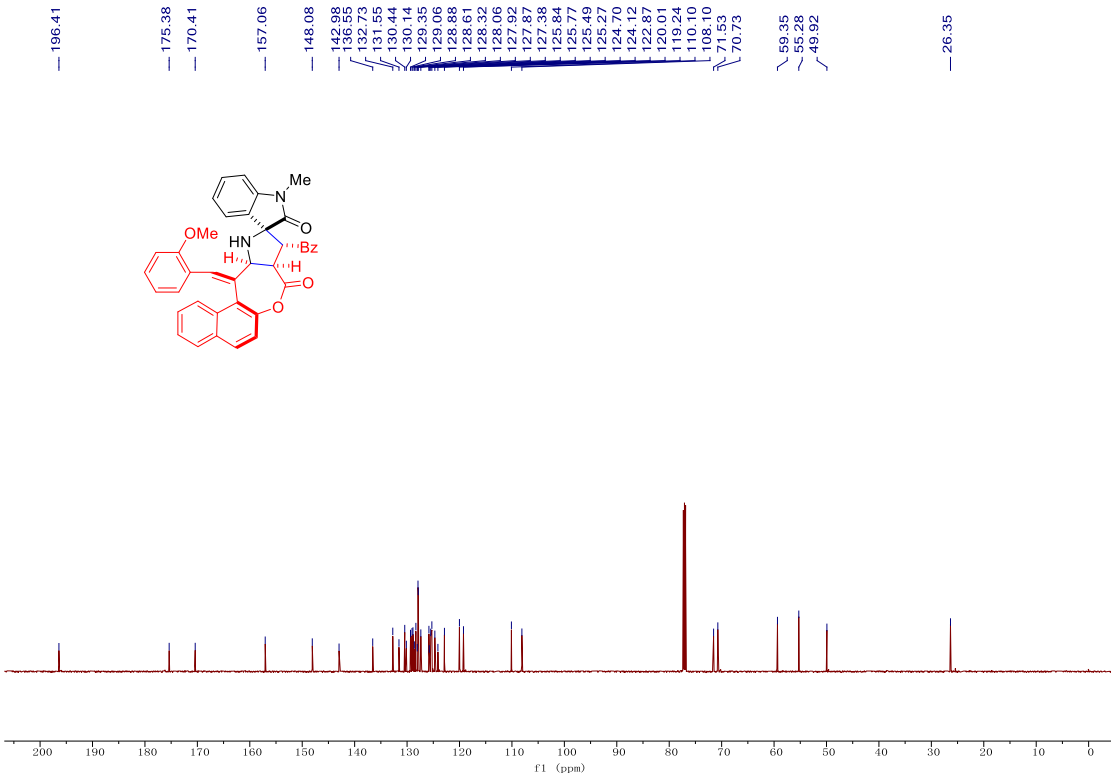
5ma


7.92 7.91 7.82 7.80 7.78 7.77 7.44 7.42 7.39 7.38 7.37 7.35 7.34 7.31 7.30 7.28 7.27 7.26 7.19 7.17 7.16 7.08 7.06 7.05 6.96 6.94 6.91 6.90 6.88 6.87 6.85 6.84 6.81 6.80 6.69 6.67 6.66 6.34 6.32 5.49 5.48 5.06 5.04 5.02 4.62 4.61 4.60 4.60 3.12 3.10 2.92
Me
N
O
HN
H
Bz
H
O
Cl
O
1.02 1.01 0.97 1.02 3.05 3.01 2.96 1.03 1.02 1.03 1.00 0.98 0.98 1.01 1.02 1.02 1.01 1.00 3.01
f1 (ppm)

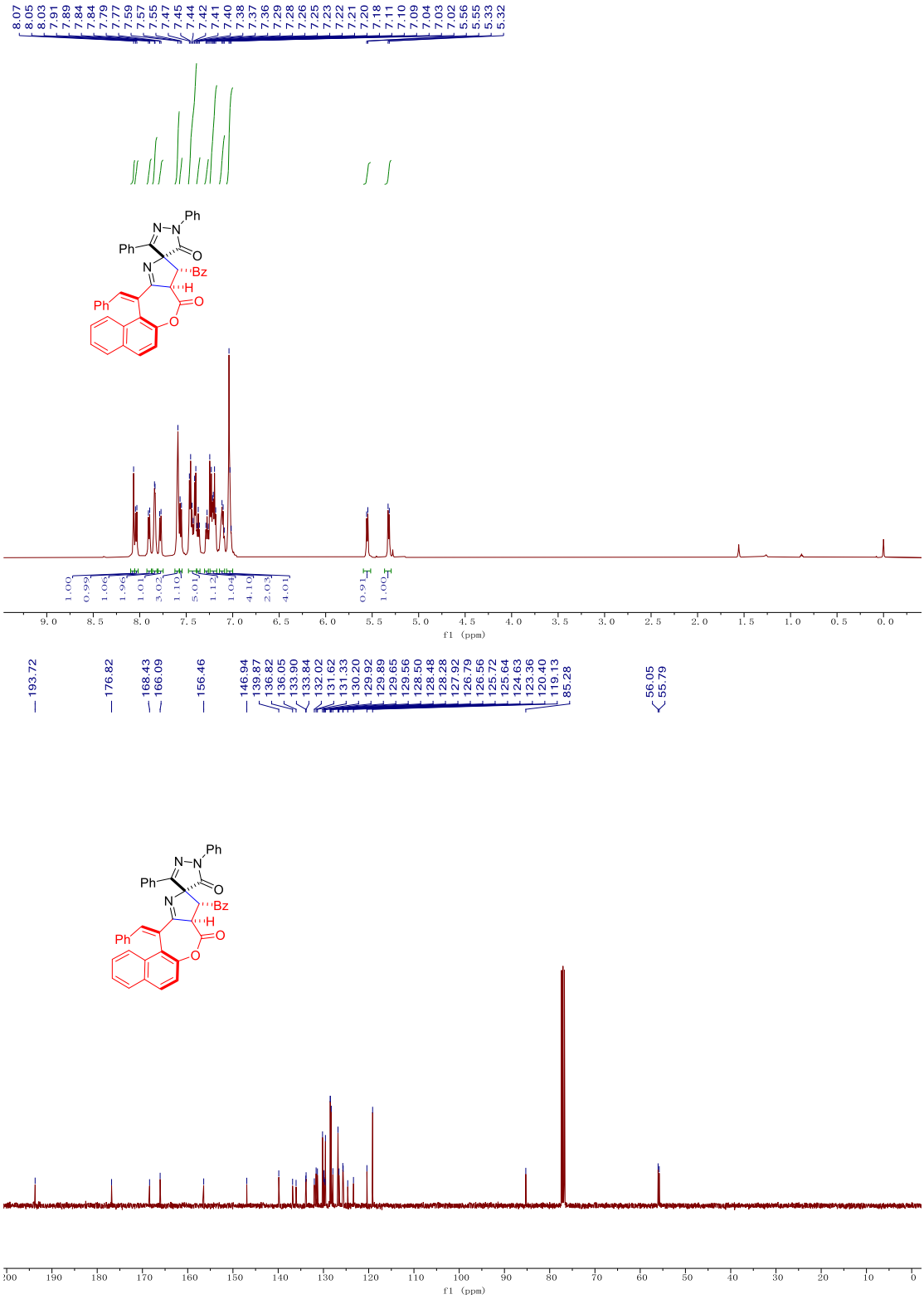

196.31 175.29 170.14 148.25 142.98 138.47 133.69 133.44 132.79 131.84 131.45 130.79 130.06 129.78 129.42 129.03 128.96 128.37 128.00 127.94 127.88 127.64 127.31 126.29 125.97 125.43 124.69 124.29 122.88 119.05 108.15 71.01 70.59 59.20 49.70 26.37
Me
N
O
HN
H
Bz
H
O
Cl
O
f1 (ppm)

5na

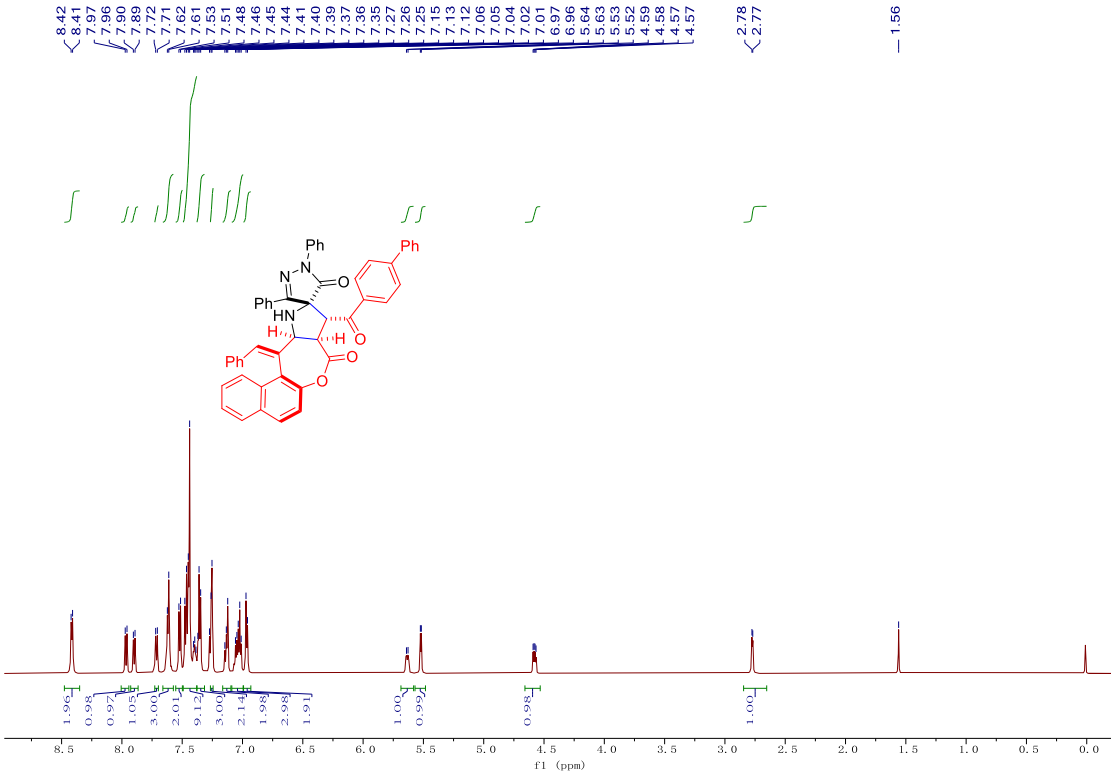

7.92 7.91 7.84 7.82 7.79 7.78 7.45 7.43 7.39 7.38 7.37 7.36 7.35 7.35 7.32 7.31 7.30 7.28 7.27 7.25 7.18 7.17 7.15 7.07 7.05 7.04 6.96 6.95 6.94 6.86 6.85 6.83 6.69 6.68 6.67 6.65 6.37 6.35 6.34 6.33 6.32 5.48 5.47 5.04 5.03 5.02 5.02 5.01 5.00 5.00 4.59 4.58 4.58 4.57 3.77 3.20 3.18 2.92
Me
N
O
HN
H
Bz
H
O
OMe
O
0.98 0.99 1.01 0.99 3.07 3.13 2.08 1.06 2.00 1.02 2.04 2.07 1.01 1.08 1.07 3.03 1.00 2.98
f1 (ppm)

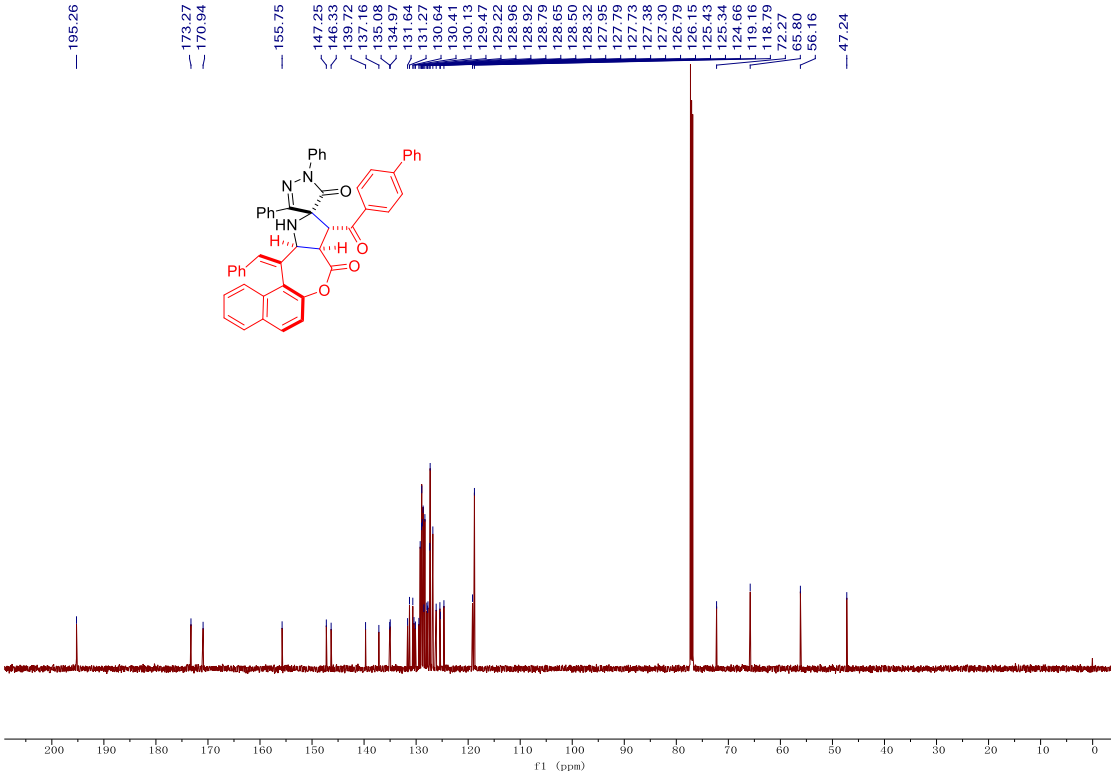

196.41 175.38 170.41 157.06 148.08 142.98 136.55 132.73 131.55 130.44 130.14 129.35 129.06 128.88 128.61 128.32 128.06 127.92 127.87 127.38 125.84 125.77 125.49 125.27 124.70 124.12 122.87 120.01 119.24 110.10 108.10 71.53 70.73 59.35 55.28 49.92 26.35
Me
N
O
HN
H
Bz
H
O
OMe
O
f1 (ppm)

6

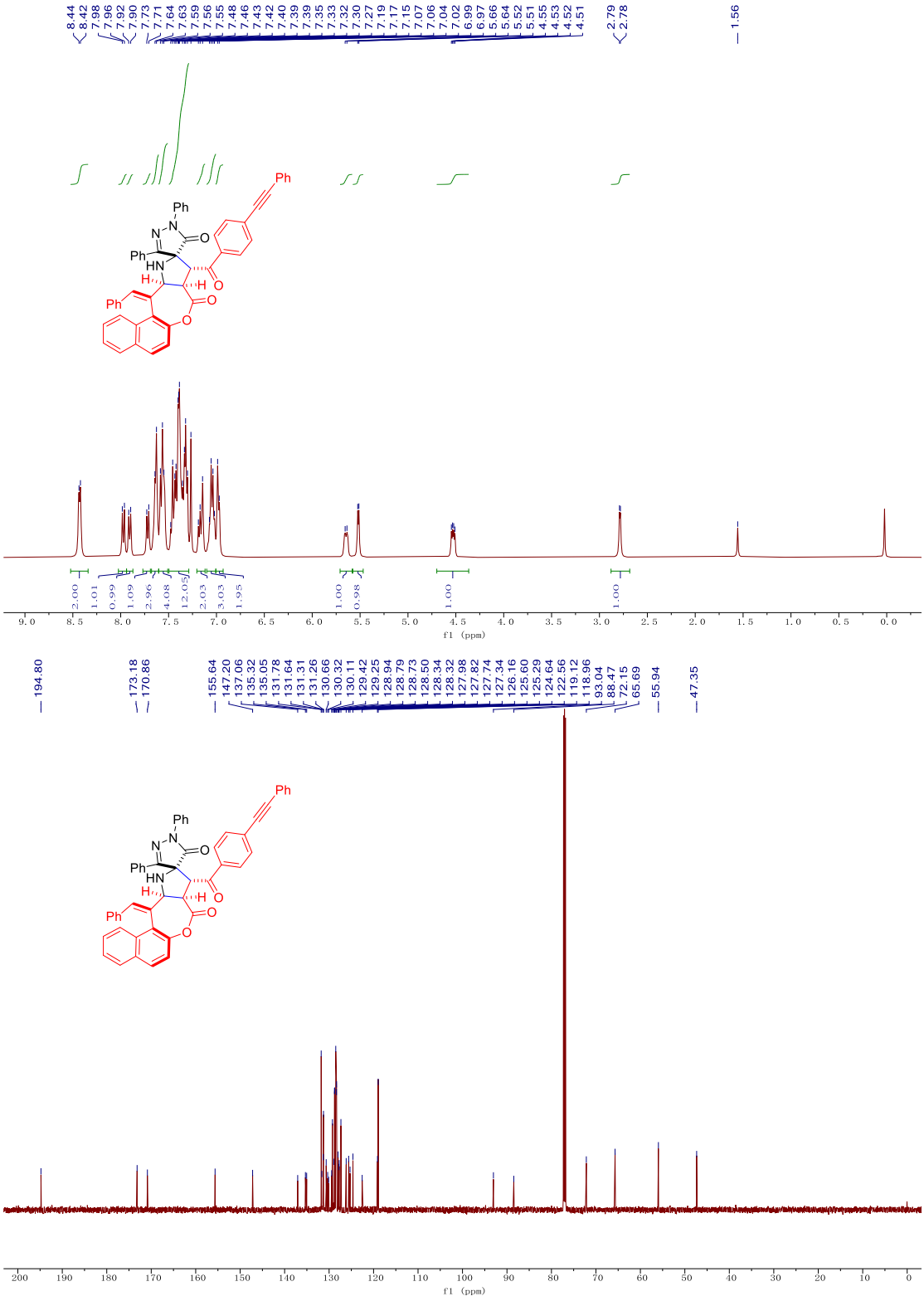

8.07 8.05 8.03 7.91 7.89 7.84 7.84 7.79 7.77 7.59 7.57 7.55 7.47 7.45 7.44 7.42 7.41 7.40 7.38 7.37 7.36 7.29 7.28 7.26 7.25 7.23 7.22 7.21 7.20 7.18 7.11 7.10 7.09 7.04 7.03 7.02 5.56 5.55 5.33 5.32
Ph
N
N
Ph
O
N
Bz
H
Ph
O
O
1.00 0.99 1.06 1.96 1.01 3.02 1.10 5.01 1.12 1.04 4.10 2.03 4.01 0.91 1.00
f1 (ppm)
193.72 176.82 168.43 166.09 156.46 146.94 139.87 136.82 136.05 133.90 133.84 132.02 131.62 131.33 130.20 129.92 129.89 129.65 129.56 128.50 128.48 128.28 127.92 126.79 126.56 125.72 125.64 124.63 123.36 120.40 119.13 85.28 56.05 55.79
f1 (ppm)

7

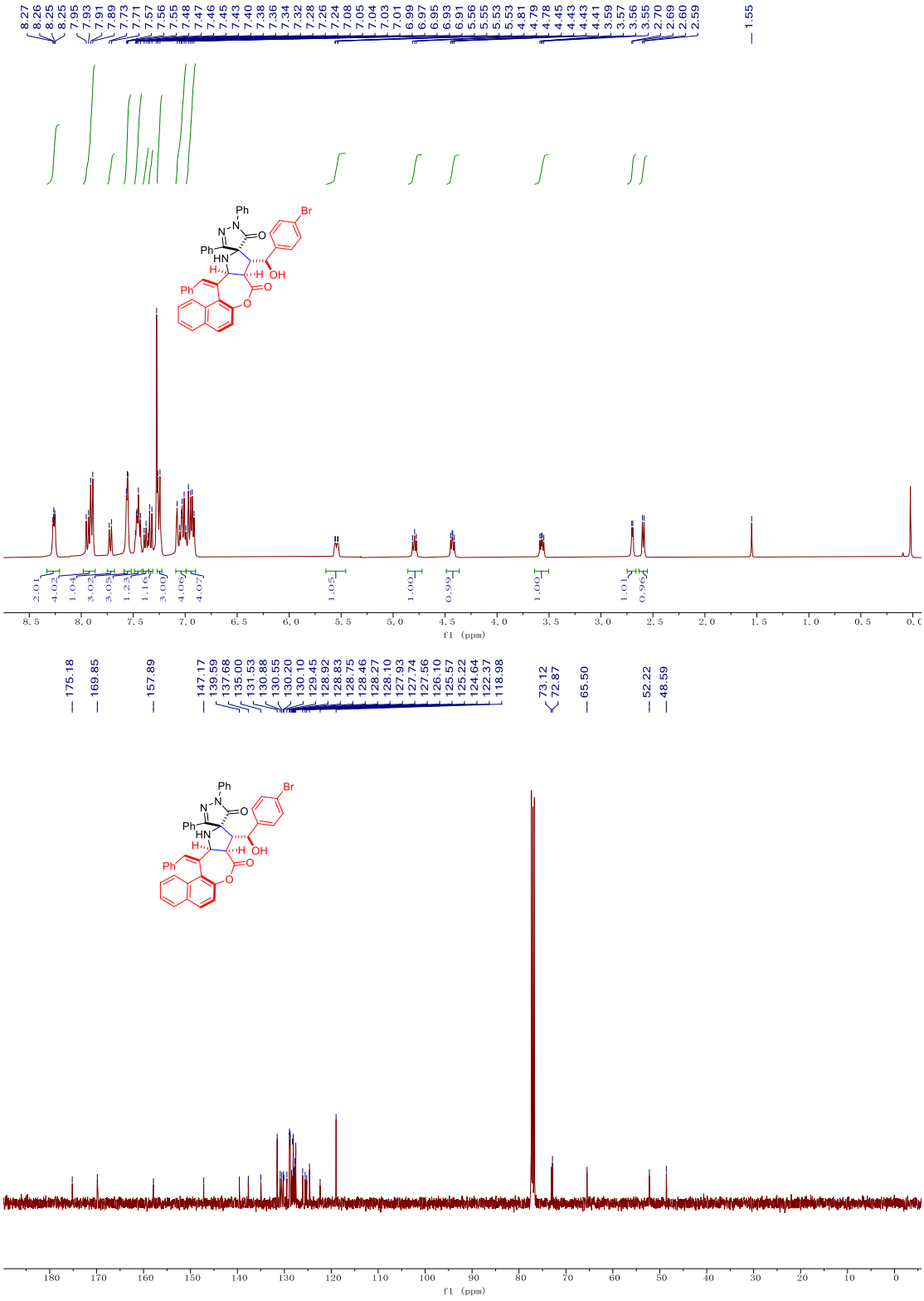

8.42
8.41
7.97
7.96
7.90
7.89
7.72
7.71
7.62
7.61
7.53
7.51
7.48
7.46
7.45
7.44
7.41
7.40
7.39
7.37
7.36
7.35
7.27
7.26
7.25
7.15
7.13
7.12
7.06
7.05
7.04
7.02
7.01
6.97
6.96
5.64
5.63
5.53
5.52
4.59
4.58
4.57
4.57
2.78
2.77
1.56
Ph
Ph
N
N
O
Ph
HN
H
H
O
Ph
O
O
1.96
0.98
0.97
1.05
3.00
2.01
9.12
3.00
2.14
1.98
2.98
1.91
1.00
0.99
0.98
1.00
f1 (ppm)


195.26
173.27
170.94
155.75
147.25
146.33
139.72
137.16
135.08
134.97
131.64
131.27
130.64
130.41
130.13
129.47
129.22
128.96
128.92
128.79
128.65
128.50
128.32
127.95
127.79
127.73
127.38
127.30
126.79
126.15
125.43
125.34
124.66
119.16
118.79
72.27
65.80
56.16
47.24
Ph
Ph
N
N
O
Ph
HN
H
H
O
Ph
O
O
f1 (ppm)

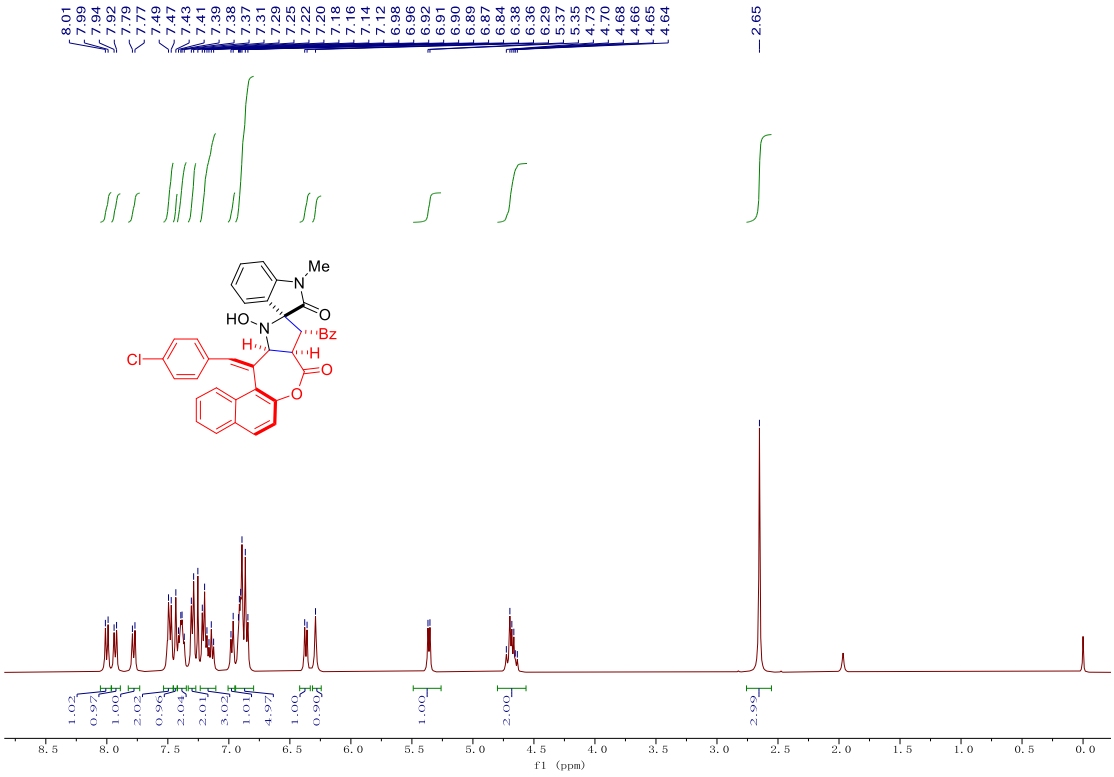
8

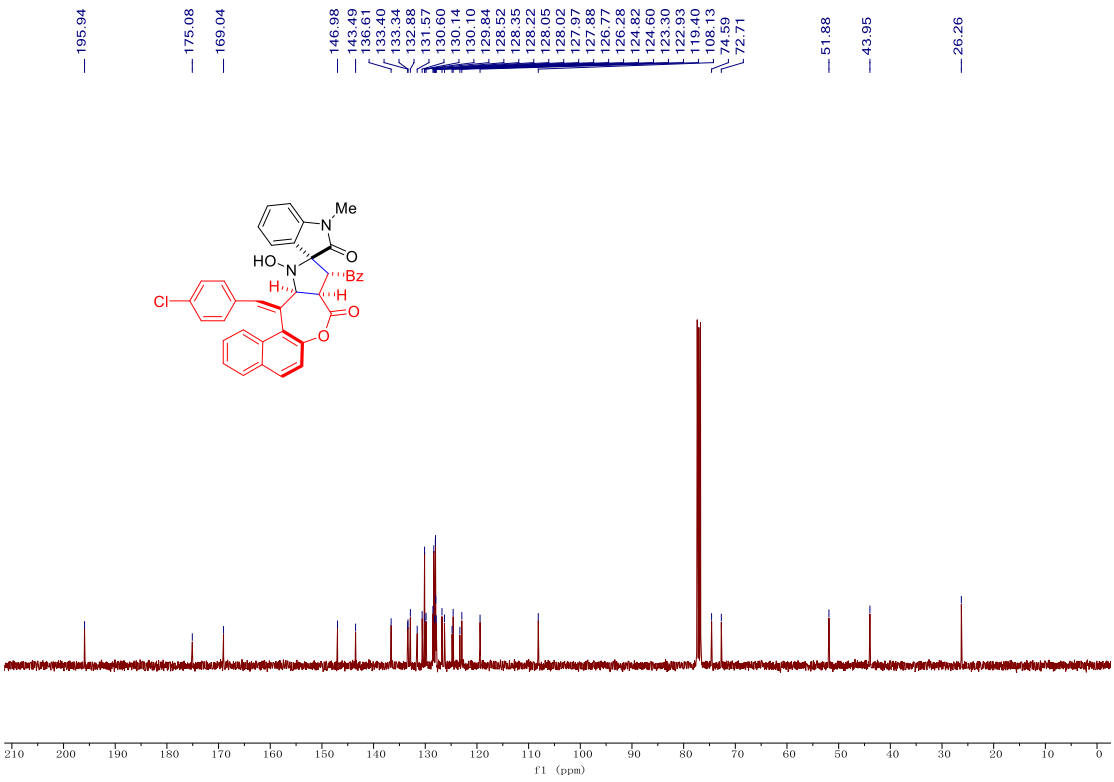

8.44
8.42
7.98
7.96
7.92
7.90
7.73
7.71
7.64
7.63
7.59
7.56
7.55
7.48
7.46
7.43
7.42
7.40
7.39
7.39
7.35
7.33
7.32
7.30
7.27
7.19
7.17
7.15
7.07
7.06
7.04
7.02
6.99
6.97
5.66
5.64
5.52
5.51
4.55
4.53
4.52
4.51
2.79
2.78
1.56
Ph
Ph
N
N
O
Ph
HN
H
H
O
O
Ph
O
2.00
1.01
0.99
1.09
2.96
4.08
12.05
2.03
3.03
1.95
1.00
0.98
1.00
1.00
f1 (ppm)
194.80
173.18
170.86
155.64
147.20
137.06
135.32
135.05
131.78
131.64
131.31
131.26
130.66
130.32
130.11
129.42
129.25
128.94
128.79
128.73
128.50
128.34
128.32
127.98
127.82
127.74
127.34
126.16
125.60
125.29
124.64
122.56
119.12
118.96
93.04
88.47
72.15
65.69
55.94
47.35
f1 (ppm)

9

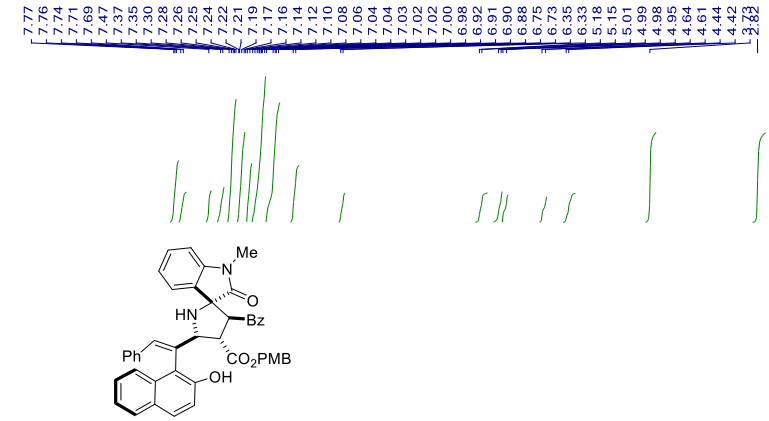

8.27 8.26 8.25 8.25 7.95 7.93 7.91 7.89 7.73 7.71 7.57 7.56 7.55 7.48 7.47 7.46 7.45 7.43 7.40 7.38 7.36 7.34 7.32 7.28 7.26 7.24 7.08 7.05 7.04 7.03 7.01 6.99 6.97 6.95 6.93 6.91 5.56 5.55 5.53 5.53 4.81 4.79 4.78 4.45 4.43 4.43 4.41 3.59 3.57 3.56 3.55 2.70 2.69 2.60 2.59 1.55
Ph
N
N
O
Ph
HN
H
H
OH
Br
Ph
O
O
2.01 4.02 1.04 3.02 3.05 1.23 1.16 3.00 4.06 4.07 1.05 1.00 0.92 1.00 1.01 0.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
175.18 169.85 157.89 147.17 139.59 137.68 135.00 131.53 130.88 130.55 130.20 130.10 129.45 128.92 128.83 128.75 128.46 128.27 128.10 127.93 127.74 127.56 126.10 125.57 125.22 124.64 122.37 118.98 73.12 72.87 65.50 52.22 48.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

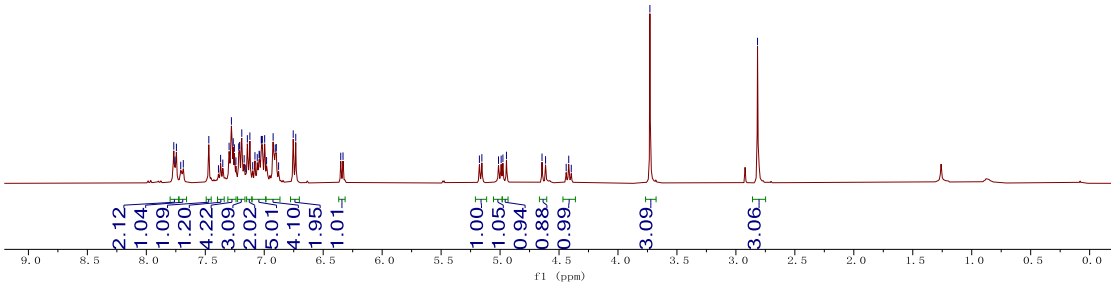
10


8.01
7.99
7.94
7.92
7.79
7.77
7.49
7.47
7.43
7.41
7.39
7.38
7.37
7.31
7.29
7.25
7.22
7.20
7.18
7.16
7.14
7.12
6.98
6.96
6.92
6.91
6.90
6.89
6.87
6.84
6.38
6.36
6.29
5.37
5.35
4.73
4.70
4.68
4.66
4.65
4.64
2.65
Me
N
O
HO
N
Bz
H
H
Cl
O
O
1.02
0.97
1.00
2.02
0.96
2.04
2.01
3.02
1.01
4.97
1.00
0.90
1.00
2.00
2.99
f1 (ppm)


195.94
175.08
169.04
146.98
143.49
136.61
133.40
133.34
132.88
131.57
130.60
130.14
130.10
129.84
128.52
128.35
128.22
128.05
128.02
127.97
127.88
126.77
126.28
124.82
124.60
123.30
122.93
119.40
108.13
74.59
72.71
51.88
43.95
26.26
Me
N
O
HO
N
Bz
H
H
Cl
O
O
f1 (ppm)

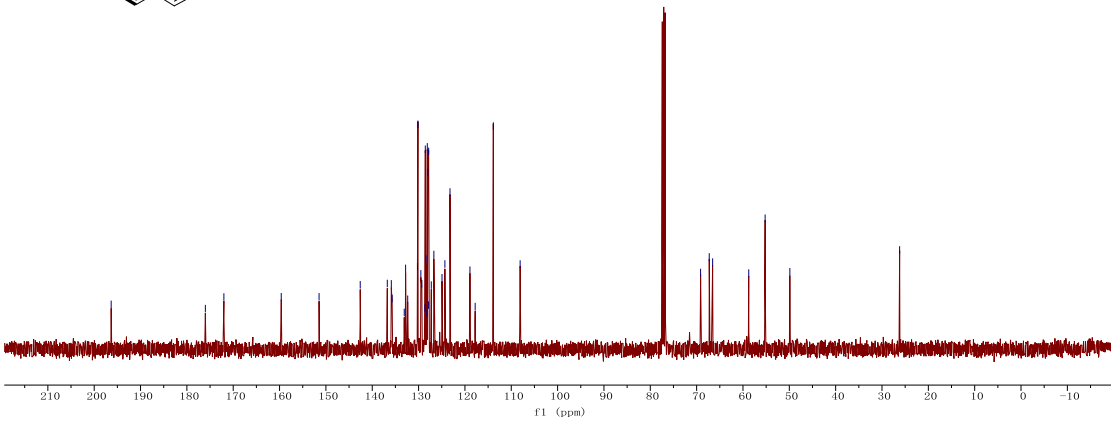
11a


Me
N
O
HN
Bz
Ph
CO2PMB
OH

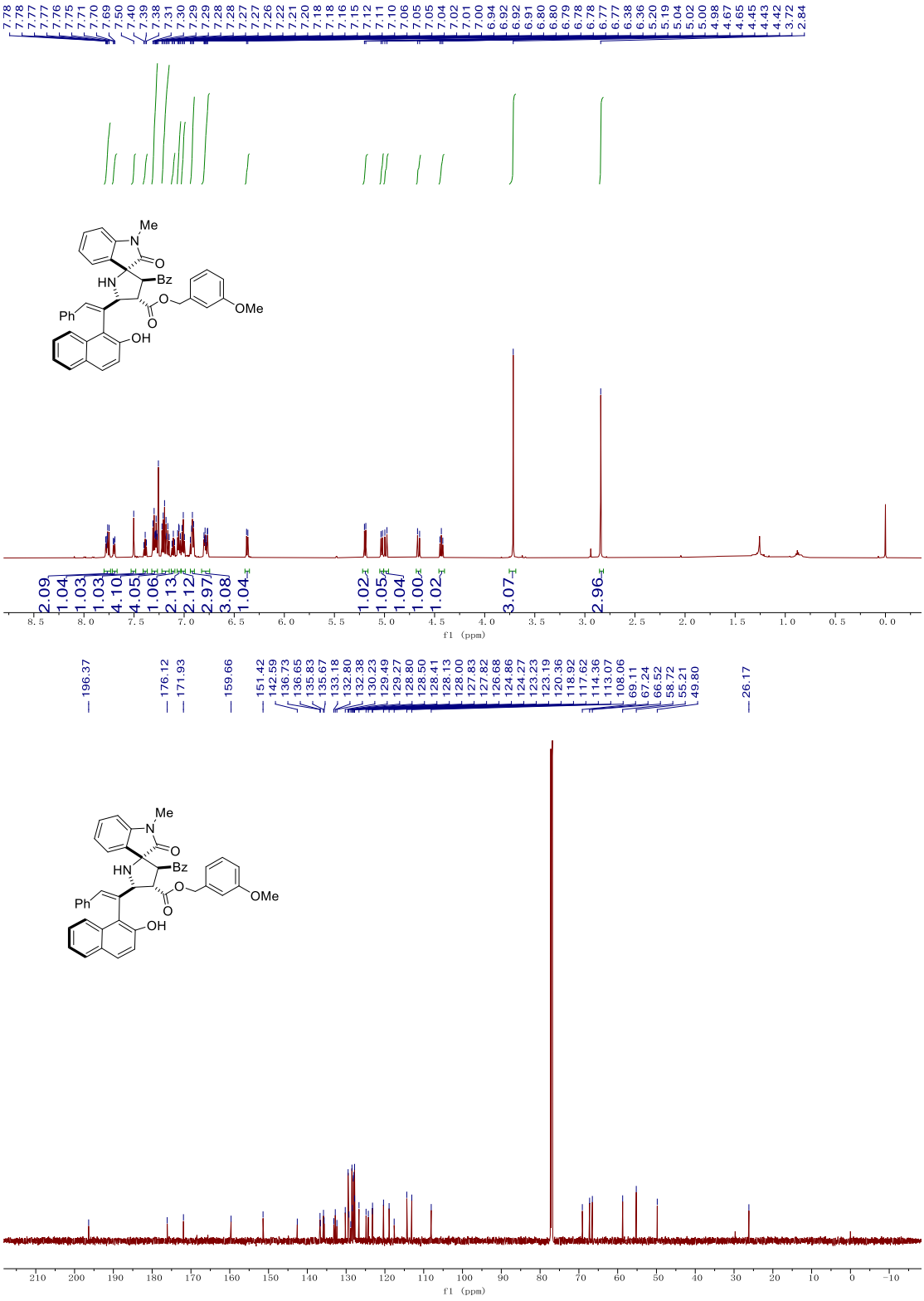

2.12
1.04
1.09
1.20
4.22
3.09
2.02
5.01
4.10
1.95
1.01
1.00
1.05
0.94
0.88
0.99
3.09
3.06
f1 (ppm)


196.34
176.01
172.01
159.64
151.47
142.59
136.75
135.88
135.70
133.09
132.80
132.35
130.23
130.14
129.51
129.29
128.63
128.55
128.41
128.20
128.12
128.01
127.88
127.83
127.26
126.70
124.94
124.33
123.22
118.92
117.79
113.87
108.09
69.15
67.28
66.55
58.75
55.22
49.88
26.20

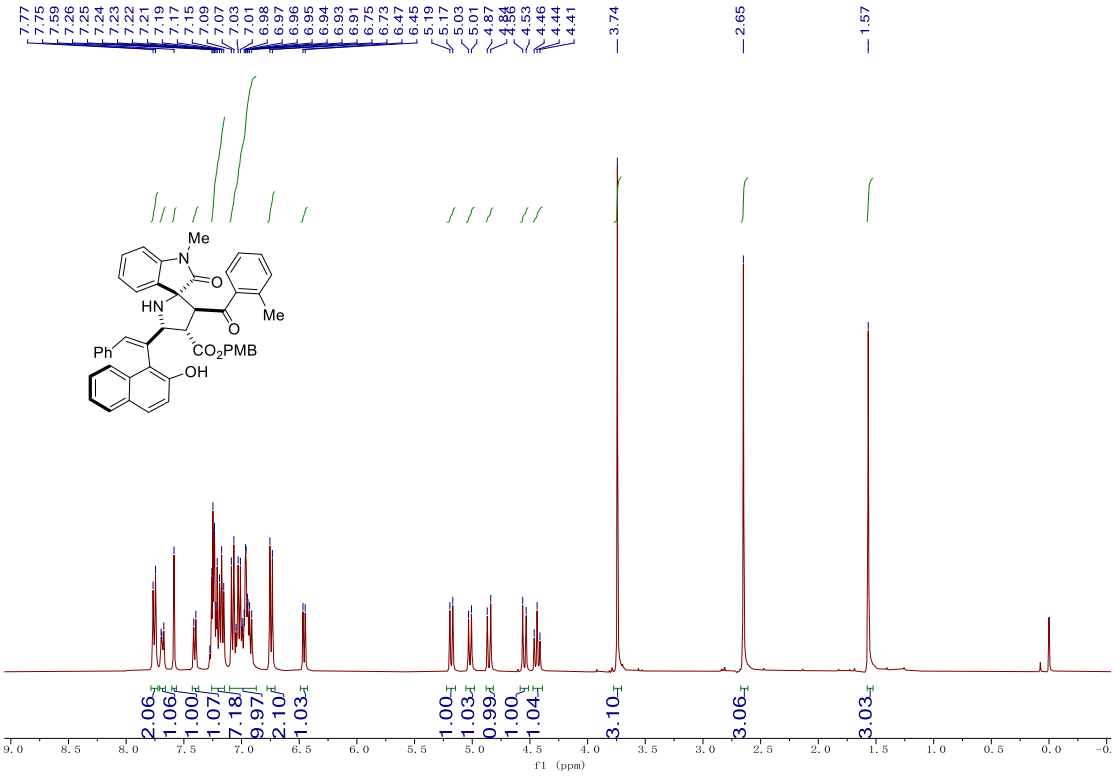

Me
N
O
HN
Bz
Ph
CO2PMB
OH

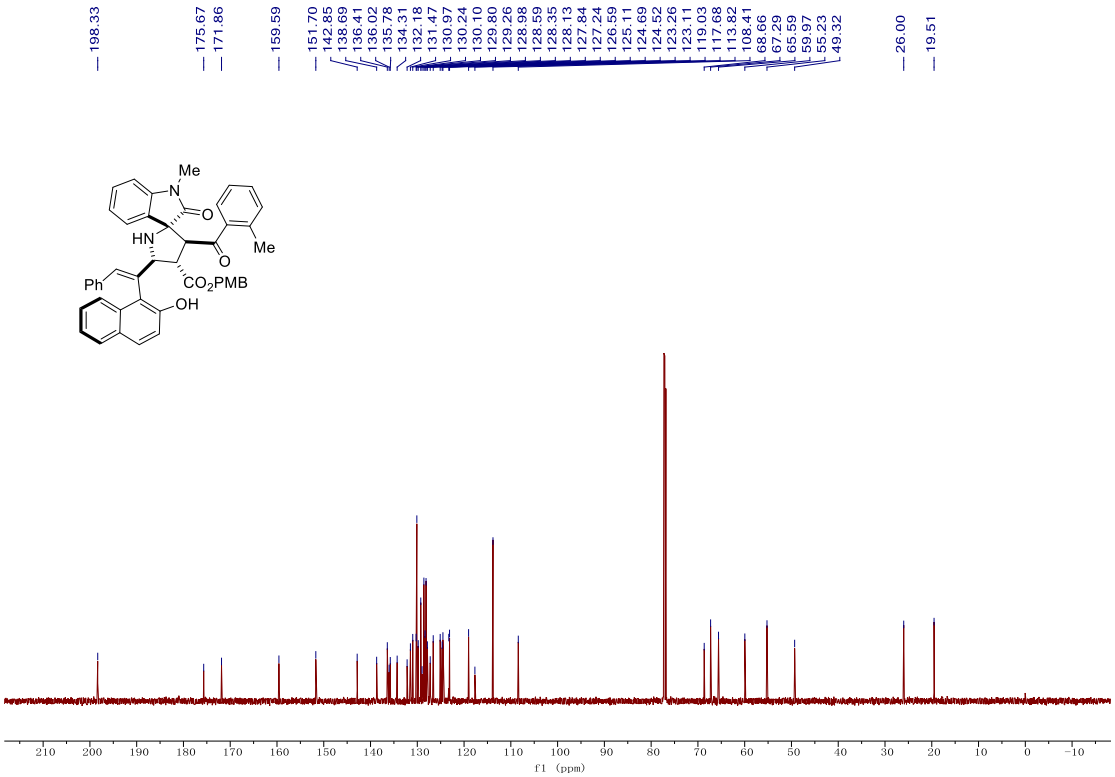

f1 (ppm)

11b

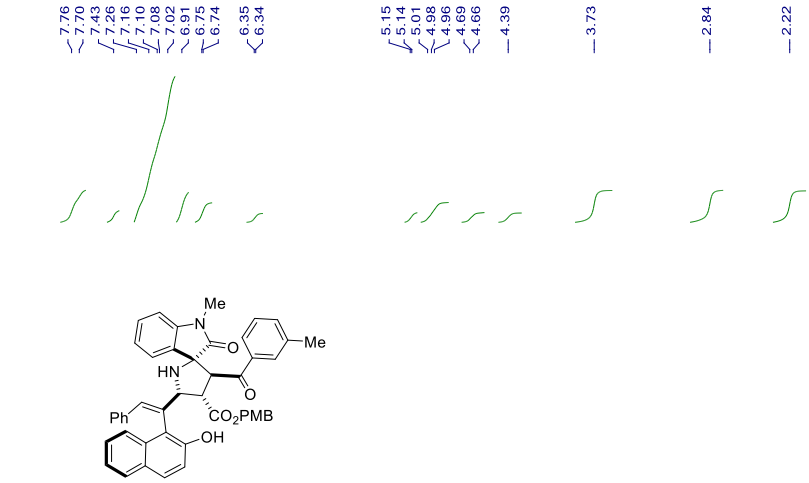

7.78 7.78 7.77 7.77 7.76 7.75 7.71 7.70 7.69 7.50 7.40 7.39 7.38 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.22 7.21 7.20 7.18 7.18 7.16 7.15 7.12 7.11 7.10 7.06 7.05 7.05 7.04 7.02 7.01 7.00 6.94 6.92 6.92 6.91 6.80 6.80 6.79 6.78 6.78 6.77 6.77 6.38 6.36 5.20 5.19 5.04 5.02 5.00 4.98 4.67 4.65 4.45 4.43 4.42 3.72 2.84
Me
N
O
HN
Bz
O
O
OMe
Ph
OH
2.09 1.04 1.03 1.03 4.10 4.05 1.06 2.13 2.12 2.97 3.08 1.04 1.02 1.05 1.04 1.00 1.02 3.07 2.96
f1 (ppm)
196.37 176.12 171.93 159.66 151.42 142.59 136.73 136.65 135.83 135.67 133.18 132.80 132.38 130.23 129.49 129.27 128.80 128.50 128.41 128.13 128.00 127.83 127.82 126.68 124.86 124.27 123.23 123.19 120.36 118.92 117.62 114.36 113.07 108.06 69.11 67.24 66.52 58.72 55.21 49.80 26.17
f1 (ppm)

11c

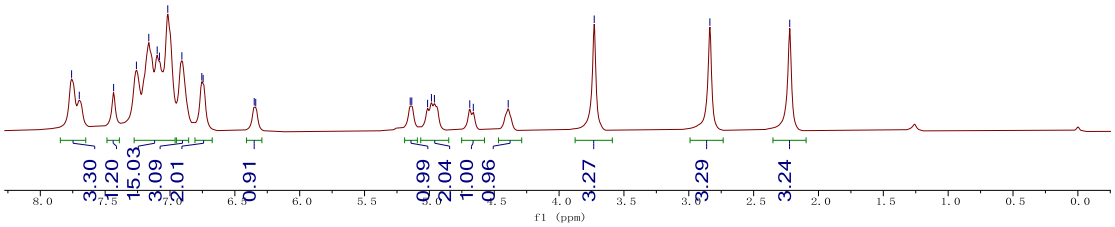

7.77
7.75
7.59
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.17
7.15
7.09
7.07
7.03
7.01
6.98
6.97
6.96
6.95
6.94
6.93
6.91
6.75
6.73
6.47
6.45
5.19
5.17
5.03
5.01
4.87
4.84
4.56
4.53
4.46
4.44
4.41
3.74
2.65
1.57
Me
N
O
HN
O
Me
Ph
CO2PMB
OH
2.06
1.06
1.00
1.07
7.18
9.97
2.10
1.03
1.00
1.03
0.99
1.00
1.04
3.10
3.06
3.03
f1 (ppm)


198.33
175.67
171.86
159.59
151.70
142.85
138.69
136.41
136.02
135.78
134.31
132.18
131.47
130.97
130.24
130.10
129.80
129.26
128.98
128.59
128.35
128.13
127.84
127.24
126.59
125.11
124.69
124.52
123.26
123.11
119.03
117.88
113.82
108.41
68.66
67.29
65.59
59.97
55.23
49.32
26.00
19.51
Me
N
O
HN
O
Me
Ph
CO2PMB
OH
f1 (ppm)

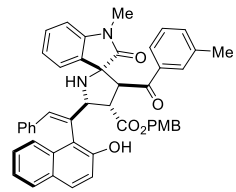
11d

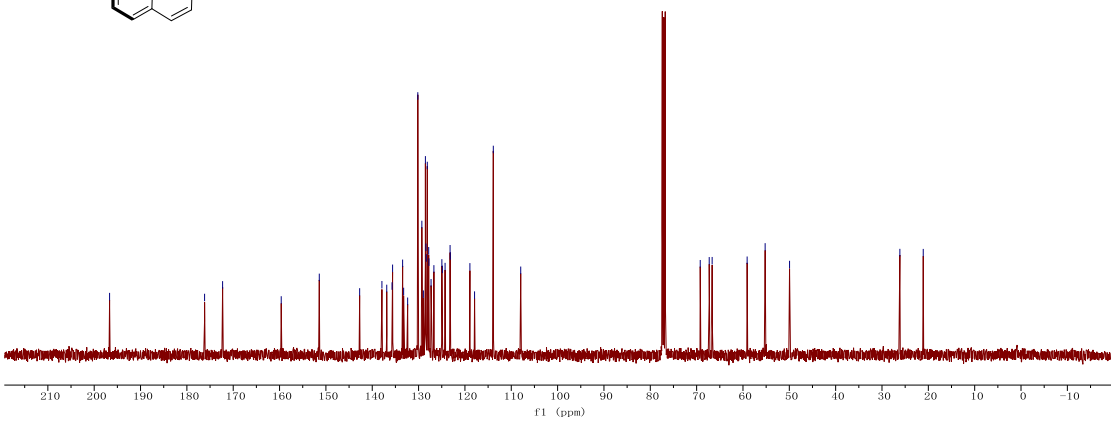

7.76
7.70
7.43
7.26
7.16
7.10
7.08
7.02
6.91
6.75
6.74
6.35
6.34
5.15
5.14
5.01
4.98
4.96
4.69
4.66
4.39
3.73
2.84
2.22

Me
N
O
Me
HN
O
Ph
CO2PMB
OH

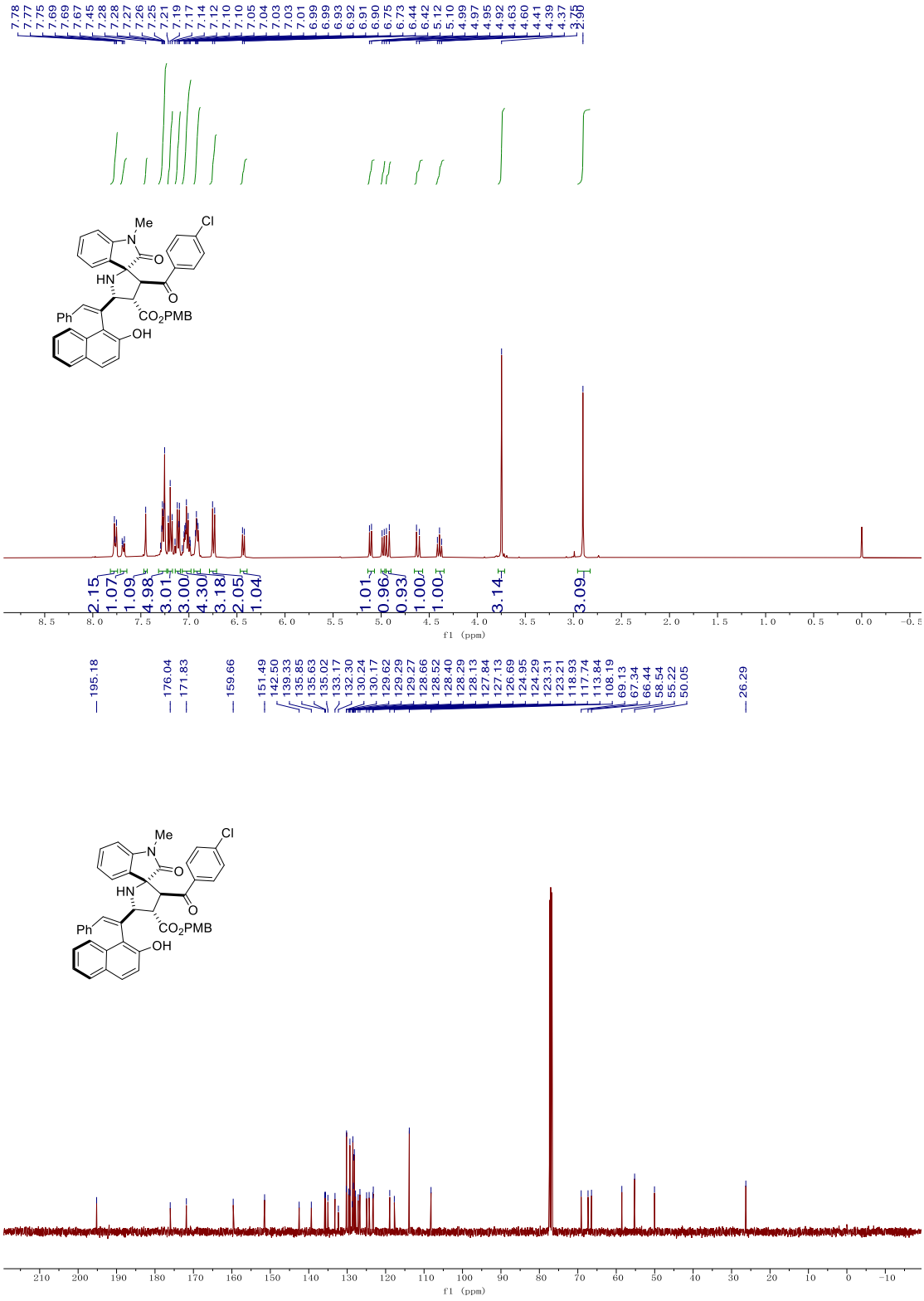

3.30
1.20
15.03
3.09
2.01
0.91
0.99
2.04
1.00
0.96
3.27
3.29
3.24
f1 (ppm)


196.68
176.18
172.29
159.64
151.43
142.72
137.91
136.87
135.73
135.61
133.45
133.23
132.36
130.17
129.29
128.97
128.53
128.41
128.34
128.12
127.82
127.77
127.31
126.70
124.98
124.87
124.28
123.20
123.16
118.93
117.92
113.88
107.96
69.22
67.29
66.65
59.10
55.22
49.95
26.14
21.10

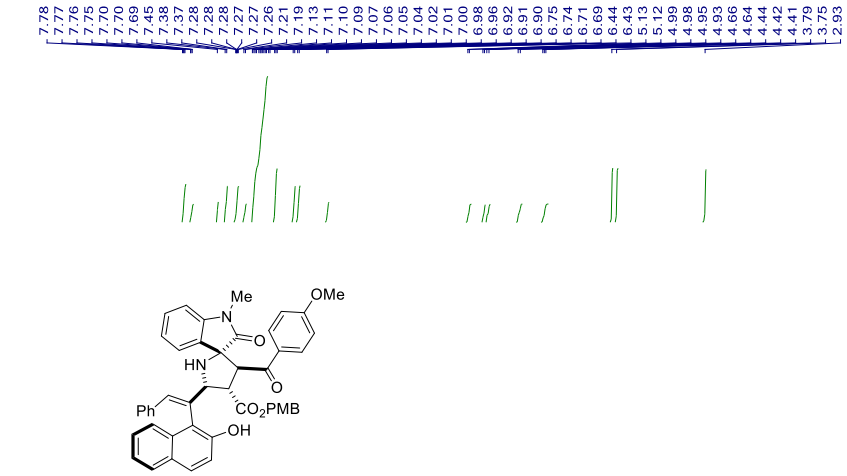

Me
N
O
Me
HN
O
Ph
CO2PMB
OH


f1 (ppm)

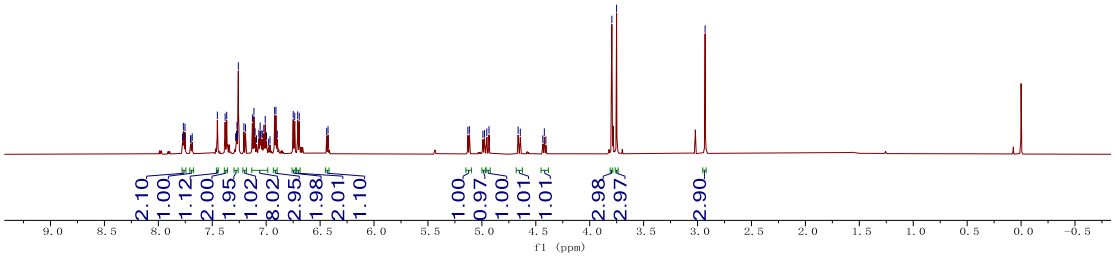
11e

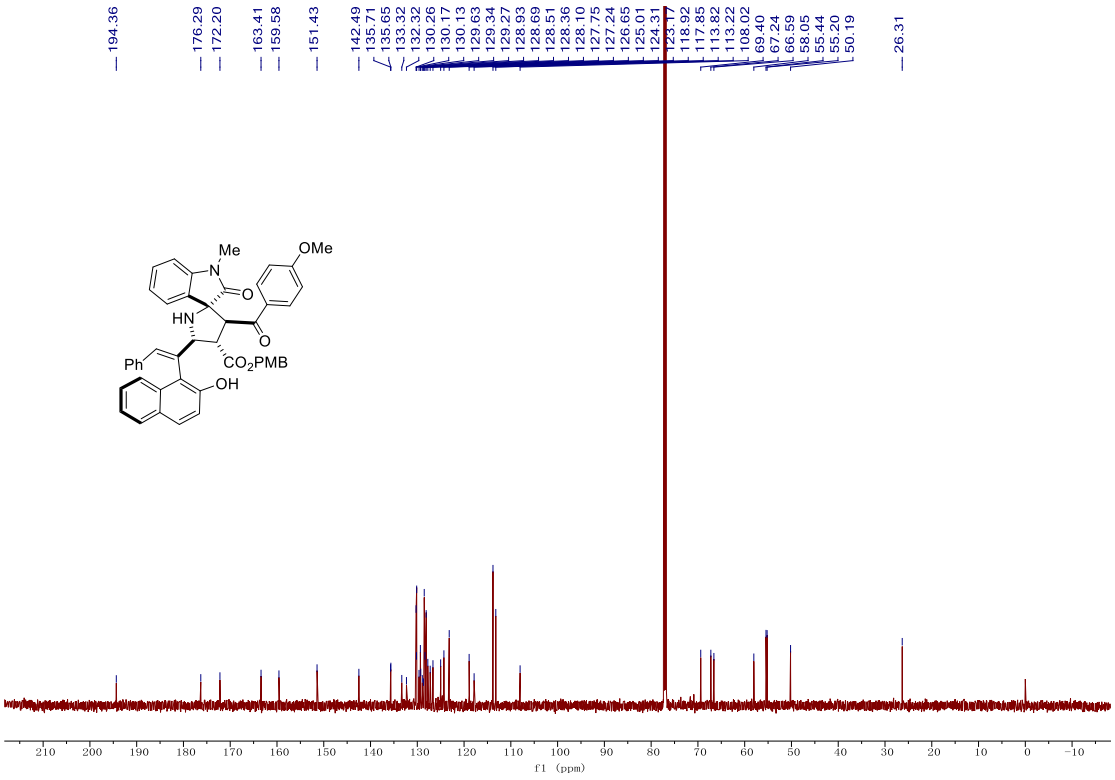


11f


7.78
7.77
7.76
7.75
7.70
7.70
7.69
7.45
7.38
7.37
7.28
7.28
7.28
7.27
7.27
7.26
7.21
7.19
7.13
7.11
7.10
7.09
7.07
7.06
7.05
7.04
7.02
7.01
7.00
6.98
6.96
6.92
6.91
6.90
6.75
6.74
6.71
6.69
6.44
6.43
5.13
5.12
4.99
4.98
4.95
4.93
4.66
4.64
4.44
4.42
4.41
3.79
3.75
2.93

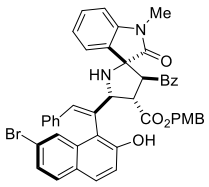
Me
OMe
N
O
HN
O
Ph
CO2PMB
OH

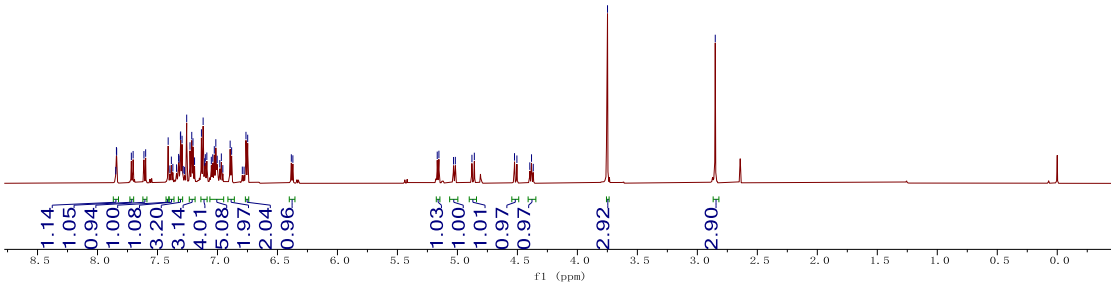

2.10
1.00
1.12
2.00
1.95
1.02
8.02
2.95
1.98
2.01
1.10
1.00
0.97
1.00
1.01
1.01
2.98
2.97
2.90
f1 (ppm)

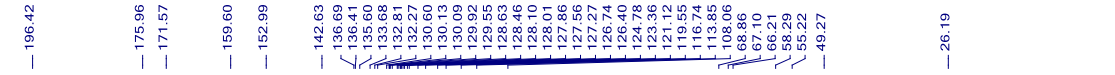

194.36
176.29
172.20
163.41
159.58
151.43
142.49
135.71
135.65
133.32
132.32
130.26
130.17
130.13
129.63
129.34
129.27
128.93
128.69
128.51
128.36
128.10
127.75
127.24
126.65
125.01
124.31
123.17
118.92
117.85
113.82
113.22
108.02
69.40
67.24
66.59
58.05
55.44
55.20
50.19
26.31
f1 (ppm)

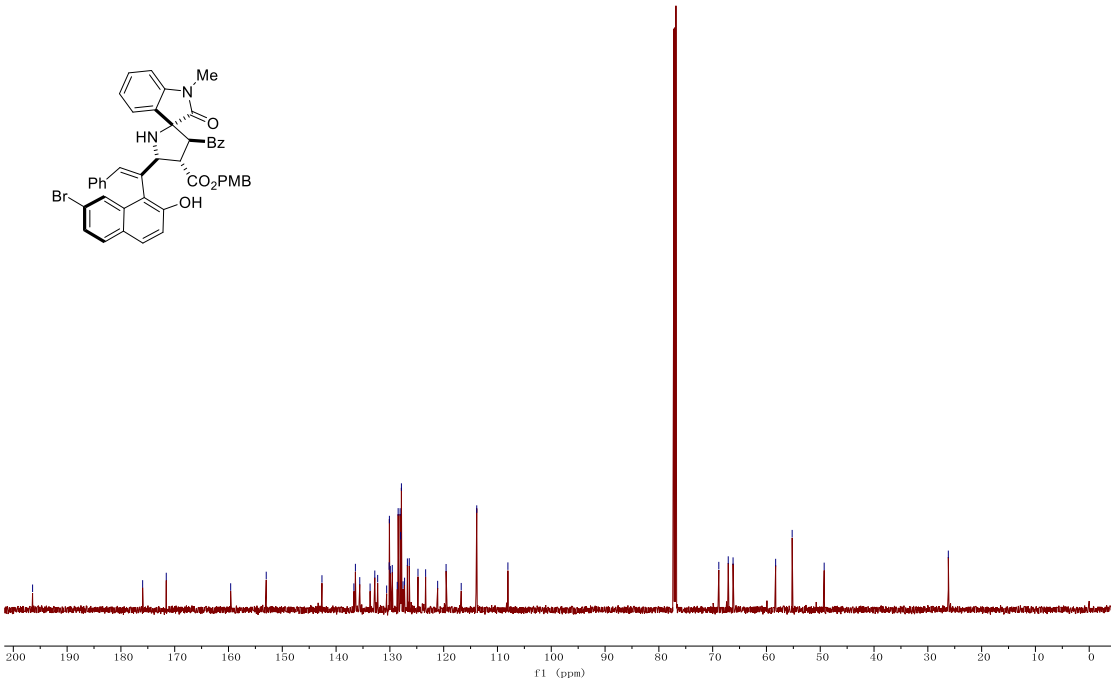
Me
OMe
N
O
HN
O
Ph
CO2PMB
OH

11g


Me
N
O
HN
Bz
Ph
CO2PMB
Br
OH


1.14
1.05
0.94
1.00
1.08
3.20
3.14
4.01
5.08
1.97
2.04
0.96
1.03
1.00
1.01
0.97
0.97
2.92
2.90
f1 (ppm)

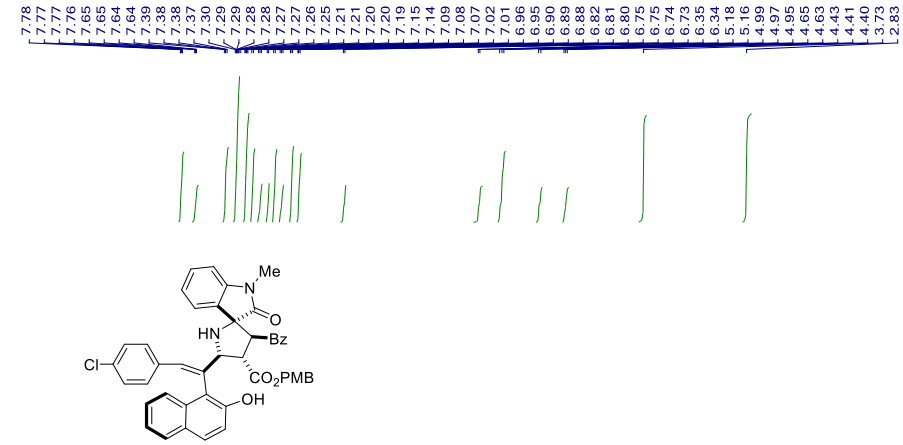



196.42
175.96
171.57
159.60
152.99
142.63
136.69
136.41
135.60
133.68
132.81
132.27
130.60
130.13
130.09
129.92
129.55
128.63
128.46
128.10
128.01
127.86
127.56
127.27
126.74
126.40
124.78
123.36
121.12
119.55
116.74
113.85
108.06
68.86
67.10
66.21
58.29
55.22
49.27
26.19

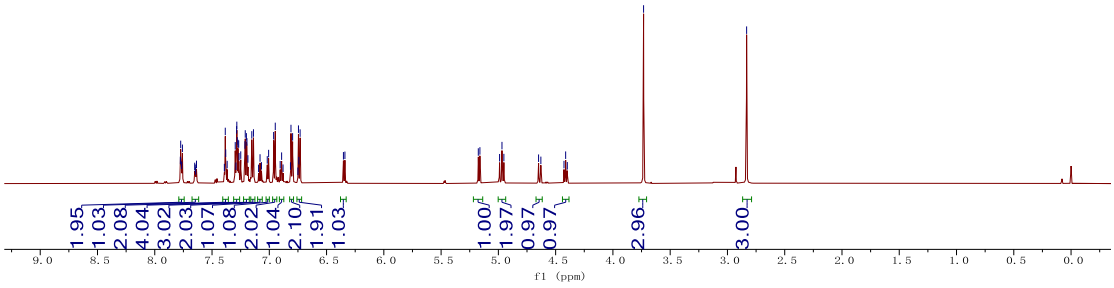
Me
N
O
HN
Bz
Ph
CO2PMB
Br
OH

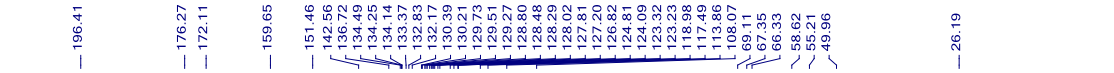
f1 (ppm)

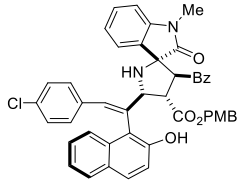
11h

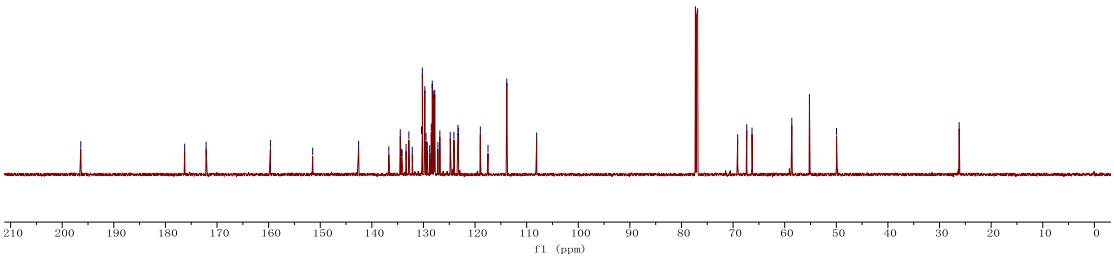

7.78
7.77
7.77
7.76
7.65
7.64
7.64
7.39
7.38
7.38
7.37
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.21
7.21
7.20
7.20
7.19
7.15
7.14
7.09
7.08
7.07
7.02
7.01
6.96
6.95
6.90
6.89
6.88
6.82
6.81
6.80
6.75
6.75
6.74
6.73
6.35
6.34
5.18
5.16
4.99
4.97
4.95
4.65
4.63
4.43
4.41
4.40
3.73
2.83

Me
N
O
HN
Bz
Cl
CO2PMB
OH

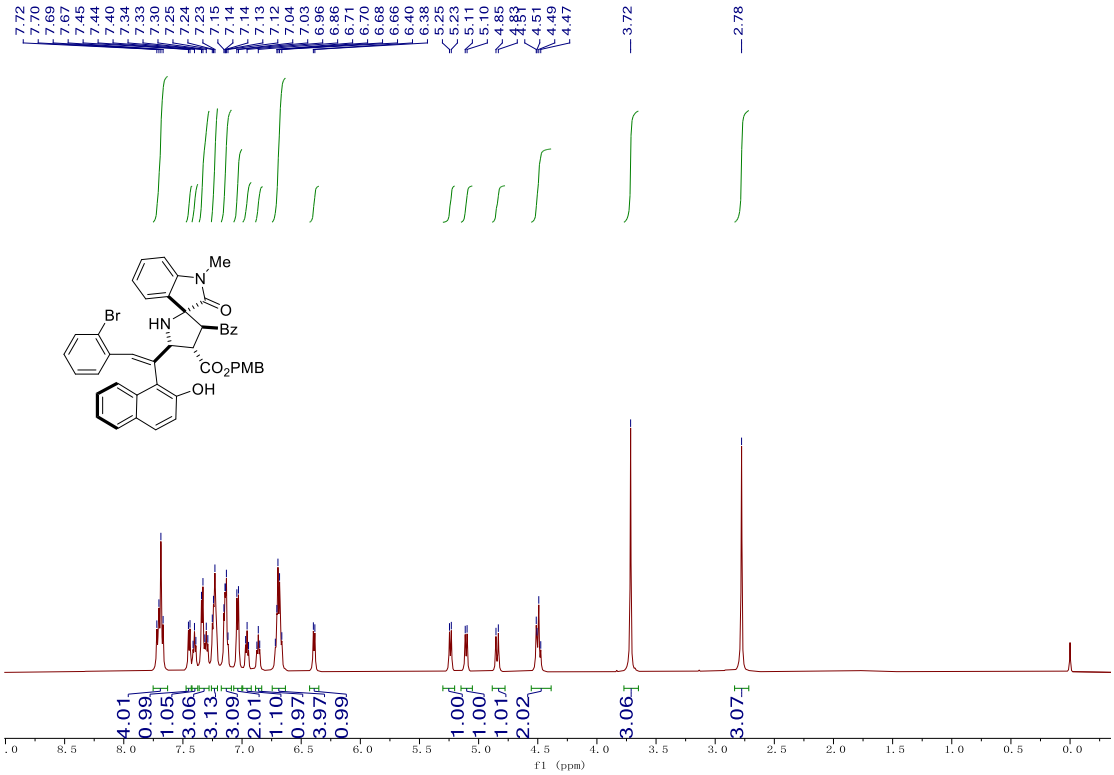

1.95
1.03
2.08
4.04
3.02
2.03
1.07
1.08
2.02
1.04
2.10
1.91
1.03
1.00
1.97
0.97
0.97
2.96
3.00
f1 (ppm)

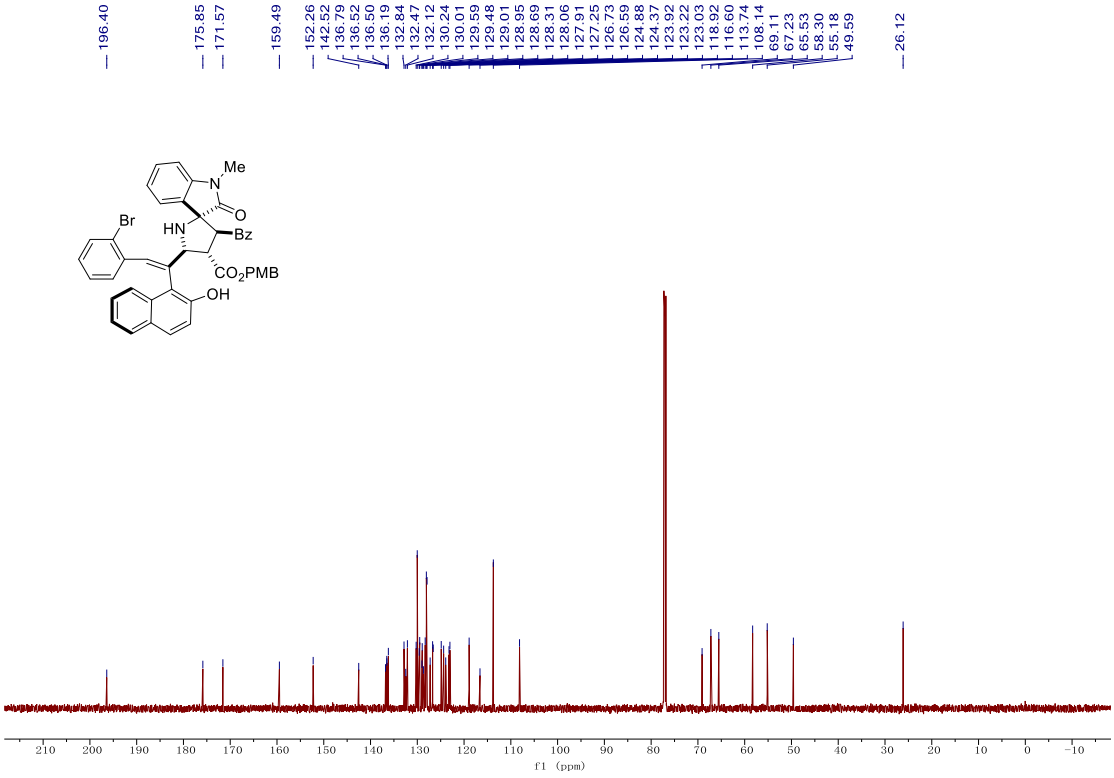

196.41
176.27
172.11
159.65
151.46
142.56
136.72
134.49
134.25
134.14
133.37
132.83
132.17
130.39
130.21
129.73
129.51
129.27
128.80
128.48
128.29
128.02
127.81
127.20
126.82
124.81
124.09
123.32
123.23
118.98
117.49
113.86
108.07
69.11
67.35
66.33
58.62
55.21
49.96
26.19


Me
N
O
HN
Bz
Cl
CO2PMB
OH

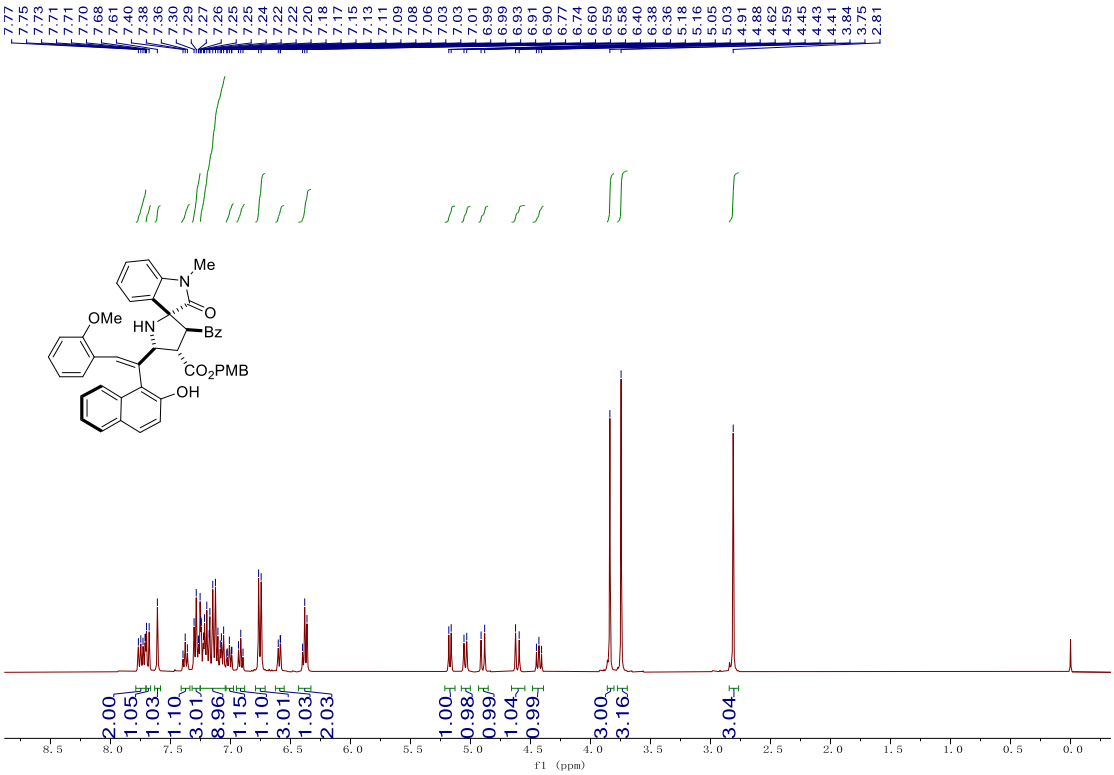

f1 (ppm)

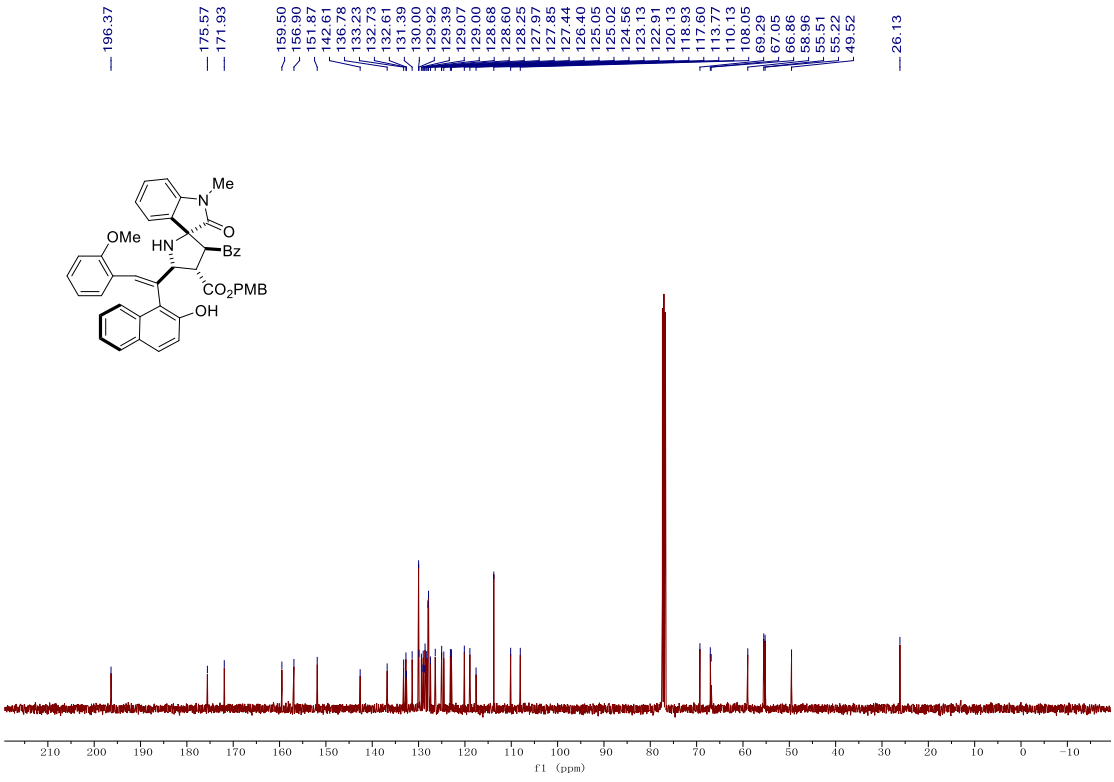
11i


7.72
7.70
7.69
7.67
7.45
7.44
7.40
7.34
7.33
7.30
7.25
7.24
7.23
7.15
7.14
7.14
7.13
7.12
7.04
7.03
6.96
6.86
6.71
6.70
6.68
6.66
6.40
6.38
5.25
5.23
5.11
5.10
4.85
4.83
4.51
4.51
4.49
4.47
3.72
2.78
Me
N
O
HN
Br
Bz
CO2PMB
OH
4.01
0.99
1.05
3.06
3.13
3.09
2.01
1.10
0.97
3.97
0.99
1.00
1.00
1.01
2.02
3.06
3.07
f1 (ppm)

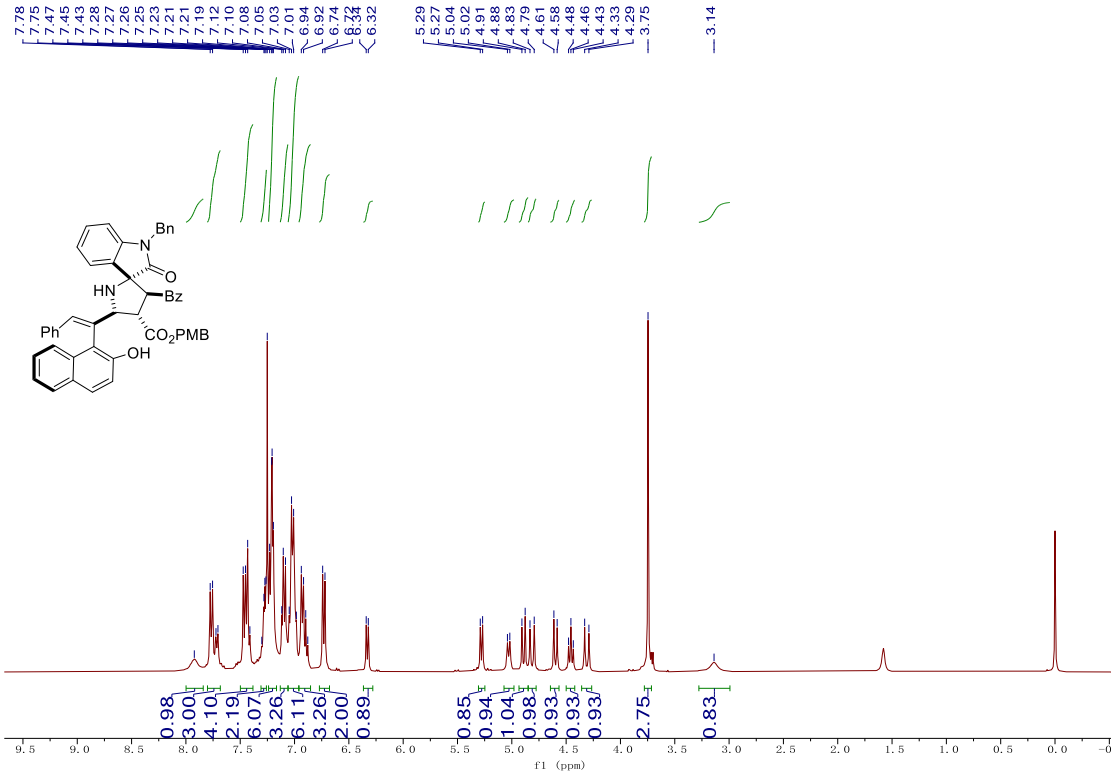

196.40
175.85
171.57
159.49
152.26
142.52
136.79
136.52
136.50
136.19
132.84
132.47
132.12
130.24
130.01
129.59
129.48
129.01
128.95
128.69
128.31
128.06
127.91
127.25
126.73
126.59
124.88
124.37
123.92
123.22
123.03
118.92
116.60
113.74
108.14
69.11
67.23
65.53
58.30
55.18
49.59
26.12
Me
N
O
HN
Br
Bz
CO2PMB
OH
f1 (ppm)

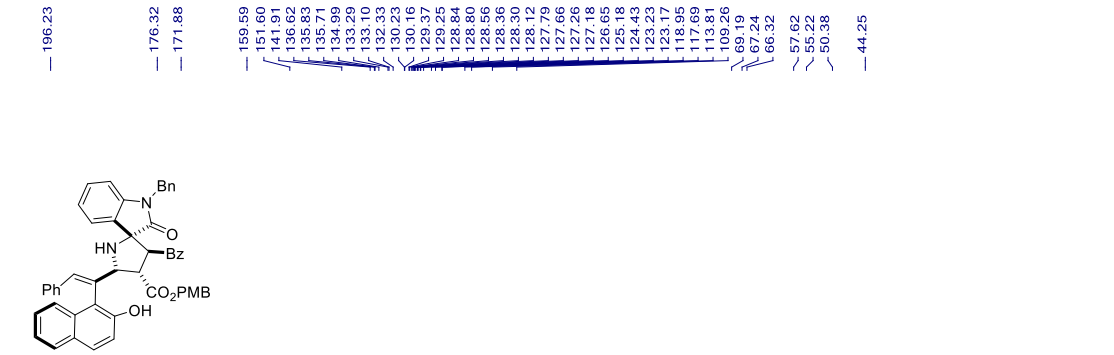
11j


7.77 7.75 7.73 7.71 7.71 7.70 7.68 7.61 7.40 7.38 7.36 7.30 7.29 7.27 7.26 7.25 7.25 7.24 7.22 7.22 7.20 7.18 7.17 7.15 7.13 7.11 7.09 7.08 7.06 7.03 7.03 7.01 6.99 6.99 6.93 6.91 6.90 6.77 6.74 6.60 6.59 6.58 6.40 6.38 6.36 5.18 5.16 5.05 5.03 4.91 4.88 4.62 4.59 4.45 4.43 4.41 3.84 3.75 2.81
Me
N
O
OMe
HN
Bz
CO2PMB
OH
2.00 1.05 1.03 1.10 3.01 8.96 1.15 1.10 3.01 1.03 2.03 1.00 0.98 0.99 1.04 0.99 3.00 3.16 3.04
f1 (ppm)


196.37 175.57 171.93 159.50 156.90 151.87 142.61 136.78 133.23 132.73 132.61 131.39 130.00 129.92 129.39 129.07 129.00 128.68 128.60 128.25 127.97 127.85 127.44 126.40 125.05 125.02 124.56 123.13 122.91 120.13 118.93 117.60 113.77 110.13 108.05 69.29 67.05 66.86 58.96 55.51 55.22 49.52 26.13
Me
N
O
OMe
HN
Bz
CO2PMB
OH
f1 (ppm)

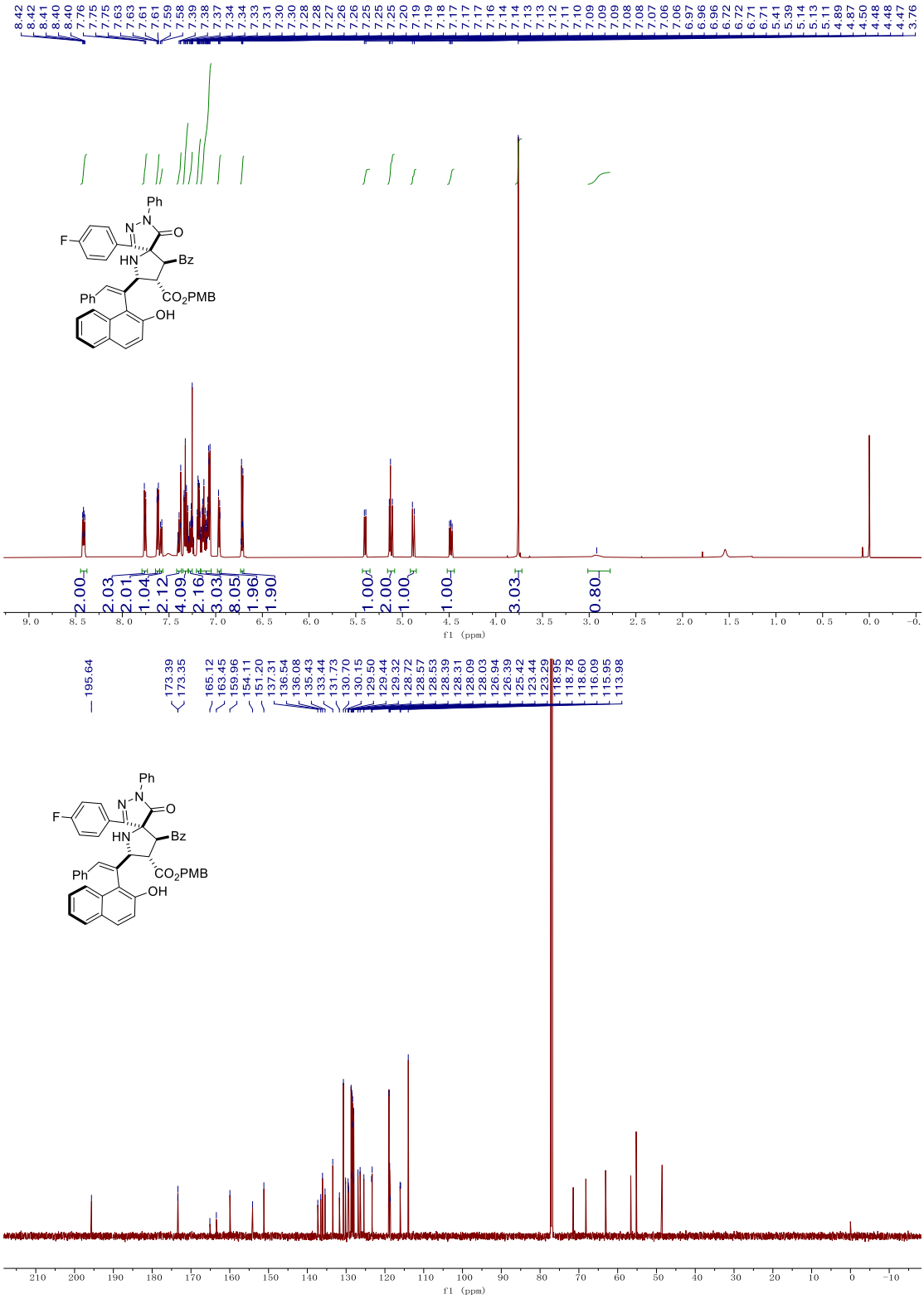
11k


7.78
7.75
7.47
7.45
7.43
7.28
7.27
7.26
7.25
7.23
7.21
7.21
7.19
7.12
7.10
7.08
7.05
7.03
7.01
6.94
6.92
6.74
6.72
6.34
6.32
5.29
5.27
5.04
5.02
4.91
4.88
4.83
4.79
4.61
4.58
4.48
4.46
4.43
4.33
4.29
3.75
3.14
Bn
N
O
HN
Bz
Ph
CO2PMB
OH
0.98
3.00
4.10
2.19
6.07
3.26
6.11
3.26
2.00
0.89
0.85
0.94
1.04
0.98
0.93
0.93
0.93
2.75
0.83
f1 (ppm)

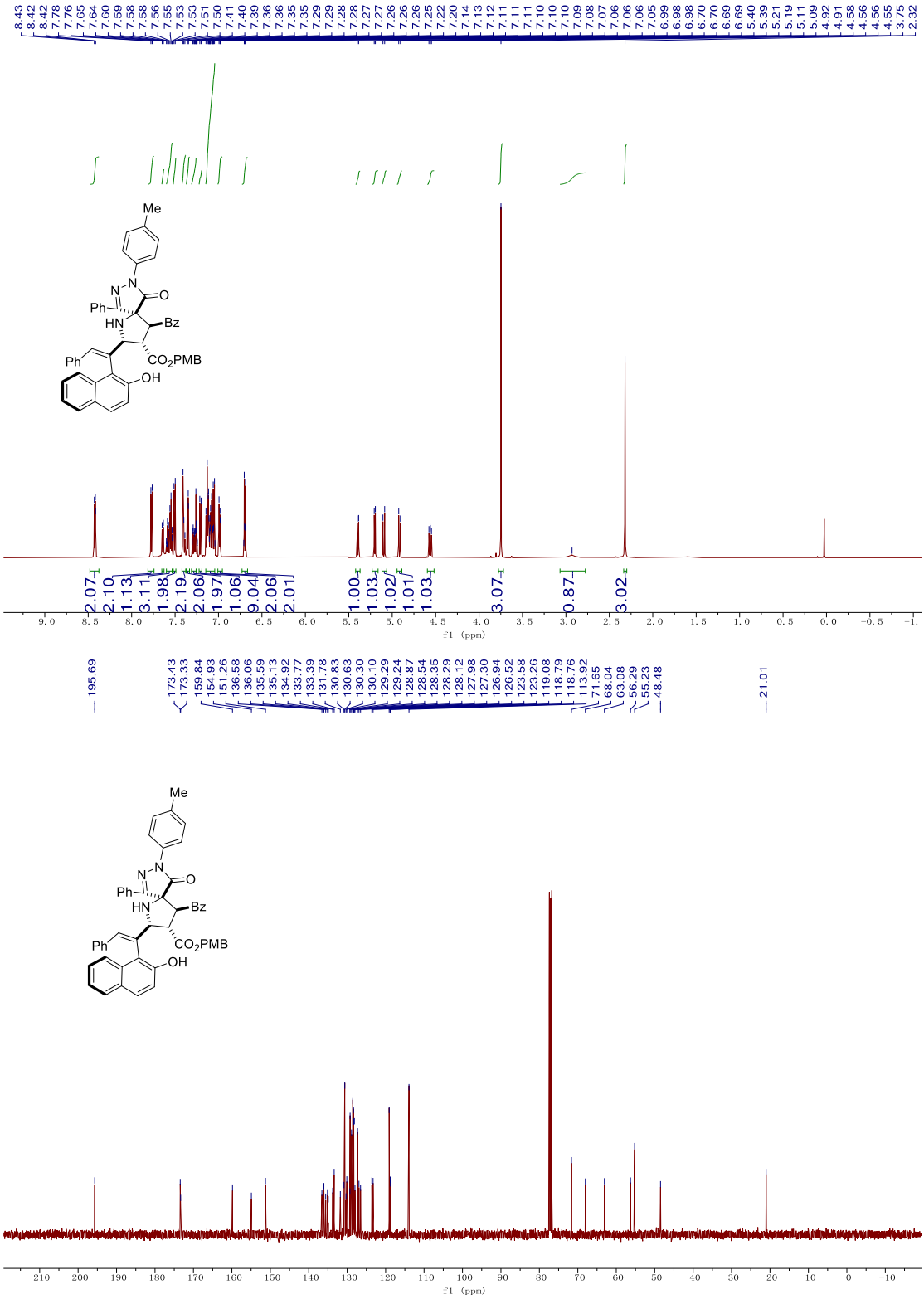

196.23
176.32
171.88
159.59
151.60
141.91
136.62
135.83
135.71
134.99
133.29
133.10
132.33
130.23
130.16
129.37
129.25
128.84
128.80
128.56
128.36
128.30
128.12
127.79
127.66
127.26
127.18
126.65
125.18
124.43
123.23
123.17
118.95
117.69
113.81
109.26
69.19
67.24
66.32
57.62
55.22
50.38
44.25

Bn
N
O
HN
Bz
Ph
CO2PMB
OH
f1 (ppm)

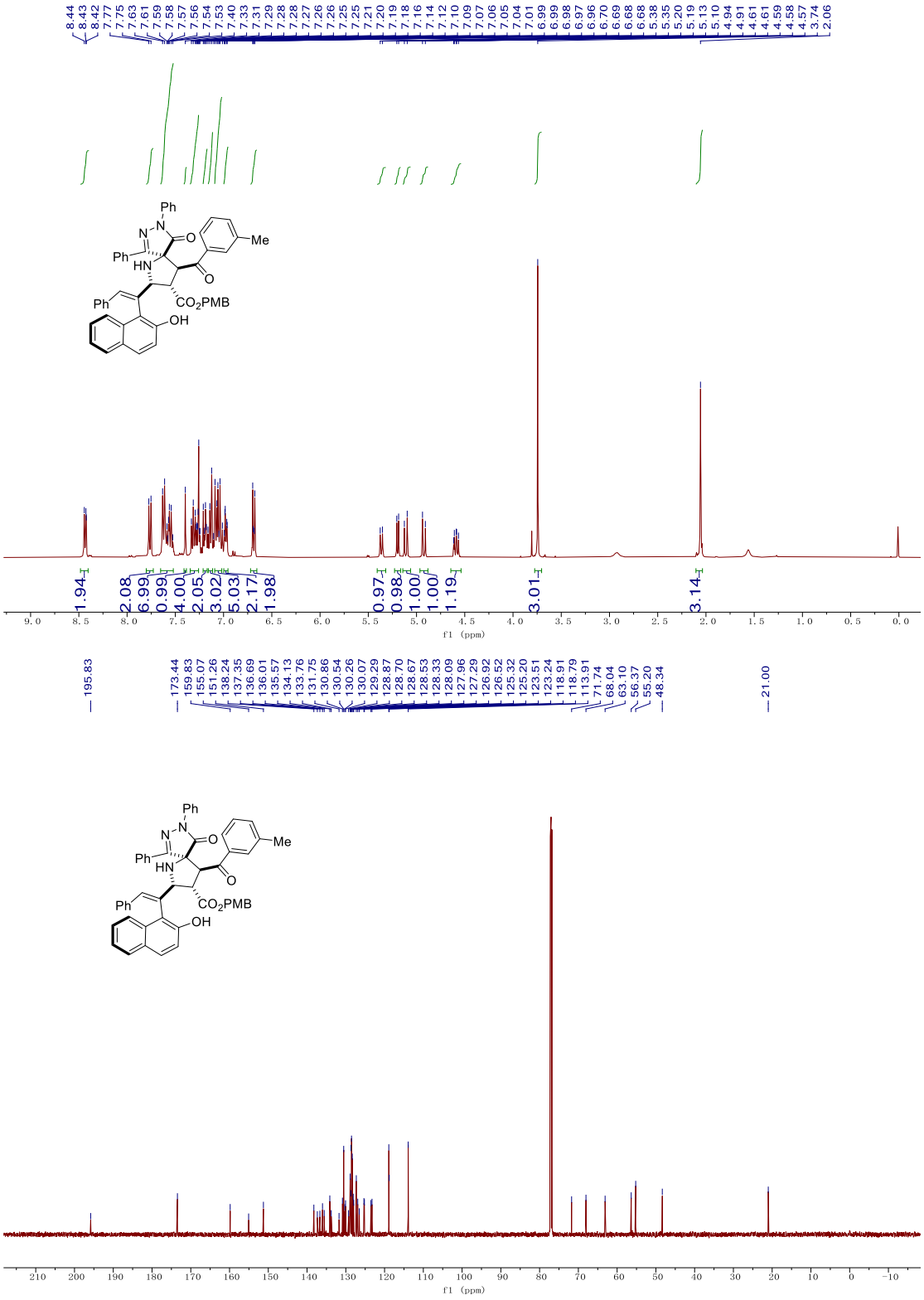
12a


8.42 8.42 8.41 8.40 8.40 7.76 7.75 7.75 7.63 7.63 7.61 7.61 7.59 7.58 7.39 7.38 7.37 7.34 7.34 7.33 7.31 7.30 7.30 7.28 7.27 7.26 7.26 7.25 7.25 7.20 7.19 7.19 7.18 7.17 7.17 7.17 7.16 7.14 7.14 7.13 7.13 7.12 7.11 7.10 7.09 7.09 7.09 7.08 7.08 7.07 7.06 6.97 6.96 6.72 6.72 6.71 5.41 5.39 5.14 5.13 5.11 4.89 4.87 4.50 4.48 4.48 4.47 3.76
Ph
N
N
O
F
HN
Bz
Ph
CO2PMB
OH
2.00 2.03 2.01 1.04 2.12 4.09 2.16 3.03 8.05 1.96 1.90 1.00 2.00 1.00 1.00 3.03 0.80
f1 (ppm)
195.64
173.39 173.35
165.12 163.45 159.96 154.11 151.20 137.31 136.54 136.08 135.43 133.44 131.73 130.70 130.15 129.50 129.44 129.32 128.72 128.57 128.53 128.39 128.31 128.09 128.03 126.94 126.39 125.42 123.44 123.29 118.85 118.78 118.60 116.09 115.95 113.98
f1 (ppm)

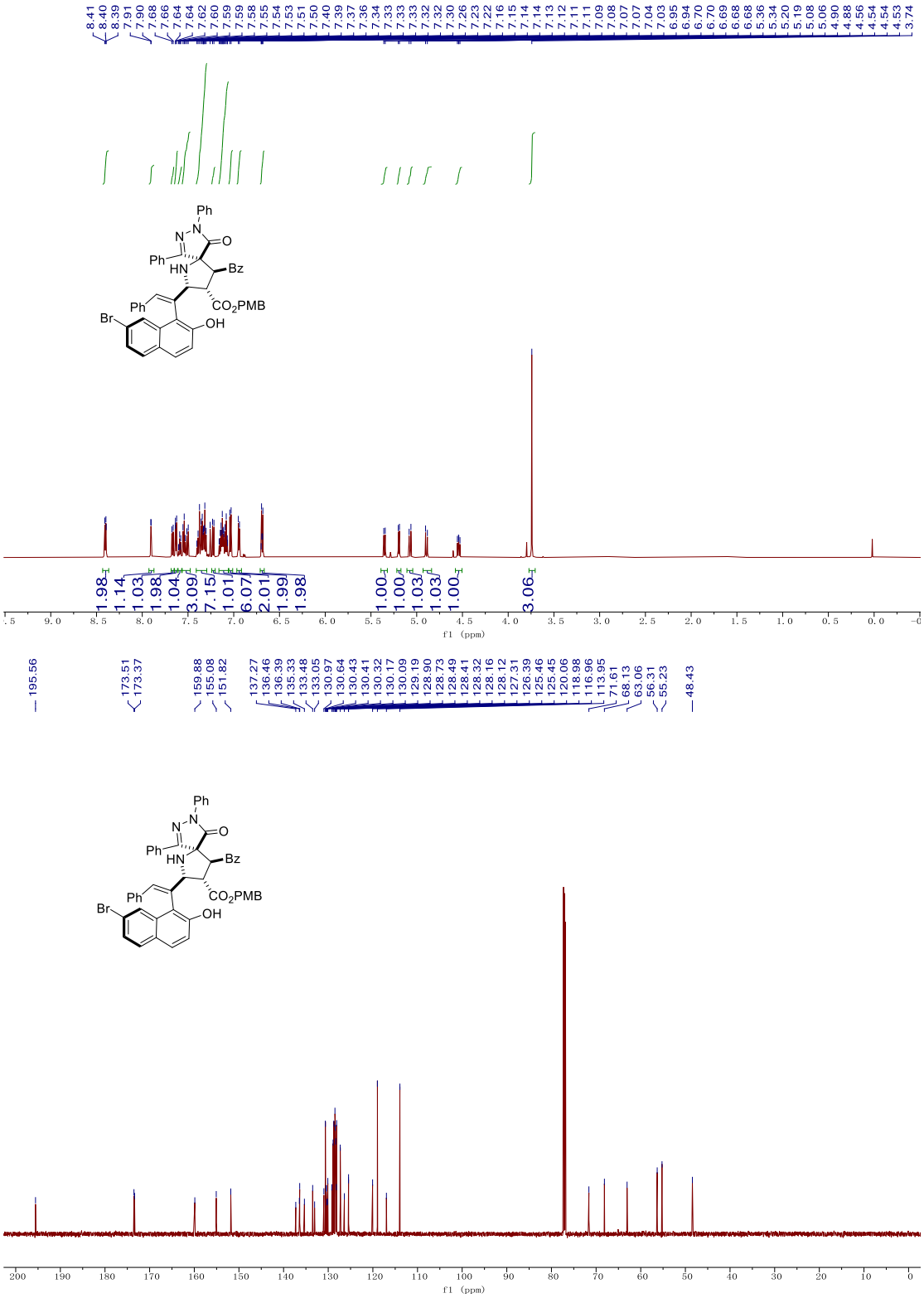
12b



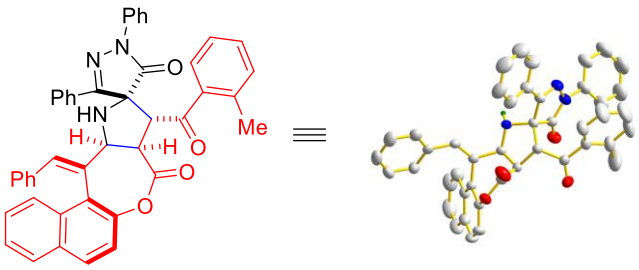
12c


8.44 8.43 8.42 7.77 7.75 7.63 7.61 7.59 7.58 7.57 7.56 7.54 7.53 7.40 7.33 7.31 7.29 7.28 7.27 7.26 7.26 7.25 7.25 7.21 7.20 7.19 7.18 7.16 7.14 7.12 7.10 7.09 7.07 7.06 7.05 7.04 7.01 6.99 6.99 6.98 6.97 6.96 6.70 6.69 6.68 6.68 5.38 5.35 5.20 5.19 5.13 5.10 4.94 4.91 4.61 4.61 4.59 4.58 4.57 3.74 2.06
Ph
N
N
O
Me
Ph
HN
O
Ph
CO2PMB
OH
1.94 2.08 6.99 0.99 4.00 2.05 3.02 5.03 2.17 1.98 0.97 0.98 1.00 1.00 1.19 3.01 3.14
f1 (ppm)
195.83 173.44 159.83 155.07 151.26 138.24 137.35 136.69 136.01 135.57 134.13 133.76 131.75 130.86 130.54 130.26 130.07 129.29 128.87 128.70 128.67 128.53 128.33 128.09 127.96 127.29 126.92 126.52 125.32 125.20 123.51 123.24 118.91 118.79 113.91 71.74 68.04 63.10 56.37 55.20 48.34 21.00
f1 (ppm)

12d


8.41 8.40 8.39 7.91 7.90 7.68 7.66 7.64 7.64 7.62 7.60 7.59 7.59 7.58 7.55 7.54 7.53 7.51 7.50 7.40 7.39 7.37 7.36 7.34 7.33 7.33 7.32 7.32 7.30 7.26 7.23 7.22 7.16 7.15 7.14 7.14 7.13 7.12 7.11 7.11 7.09 7.08 7.07 7.07 7.04 7.03 6.95 6.94 6.70 6.70 6.69 6.68 6.68 5.36 5.34 5.20 5.19 5.08 5.06 4.90 4.88 4.56 4.54 4.54 4.53 3.74
Ph
N
N
O
Ph
HN
Bz
Ph
CO2PMB
Br
OH
1.98 1.14 1.03 1.98 1.04 3.09 7.15 1.01 6.07 2.01 1.99 1.98 1.00 1.00 1.03 1.03 1.00 3.06
f1 (ppm)
195.56 173.51 173.37 159.88 155.08 151.82 137.27 136.46 136.39 135.33 133.48 133.05 130.97 130.64 130.43 130.41 130.32 130.17 130.09 129.19 128.90 128.73 128.49 128.41 128.32 128.16 128.12 127.31 126.39 125.46 125.45 120.06 118.98 116.96 113.95 71.61 68.13 63.06 56.31 55.23 48.43
f1 (ppm)

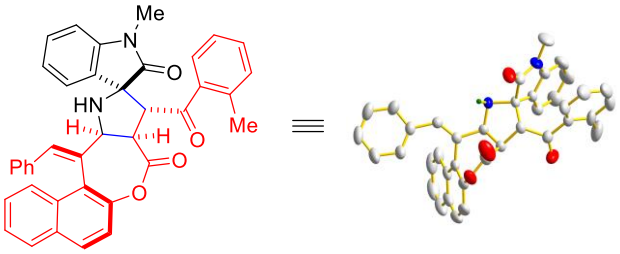
8. X-ray crystal structure of 3ba and 5ba



X-ray crystal structure of **3ba**

CCDC: 2234269

Identification code	1
Empirical formula	$C_{45}H_{33}N_3O_4$
Formula weight	679.74
Temperature/K	296.0
Crystal system	triclinic
Space group	P-1
a/Å	9.5254(9)
b/Å	11.8656(11)
c/Å	17.5066(16)
α/°	86.314(2)
β/°	80.905(2)
γ/°	81.884(2)
Volume/Å^3	1932.4(3)
Z	2
ρ_{calc}g/cm^3	1.168
μ/mm^{-1}	0.075
F(000)	712.0
Crystal size/mm^3	0.26 × 0.23 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 49.996
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	25538
Independent reflections	6696 [R_{int} = 0.0548, R_{sigma} = 0.0550]
Data/restraints/parameters	6696/432/536
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0770, wR_2 = 0.2227
Final R indexes [all data]	R_1 = 0.1104, wR_2 = 0.2382
Largest diff. peak/hole / e Å^{-3}	0.29/-0.26



X-ray crystal structure of **5ba**

CCDC: 2286710

Identification code	1
Empirical formula	$C_{39}H_{30}N_2O_4$
Formula weight	590.65
Temperature/K	263.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.0367(14)
b/Å	15.1484(18)
c/Å	17.888(2)
α/°	90
β/°	96.818(3)
γ/°	90
Volume/Å^3	3507.6(7)
Z	4
ρ_{calc}g/cm^3	1.118
μ/mm^{-1}	0.073
F(000)	1240.0
Crystal size/mm^3	0.28 × 0.26 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.138 to 50
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	48750
Independent reflections	6146 [R_{int} = 0.0489, R_{sigma} = 0.0272]
Data/restraints/parameters	6146/66/412
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0748, wR_2 = 0.2397
Final R indexes [all data]	R_1 = 0.0919, wR_2 = 0.2512
Largest diff. peak/hole / e Å^{-3}	0.62/-0.34